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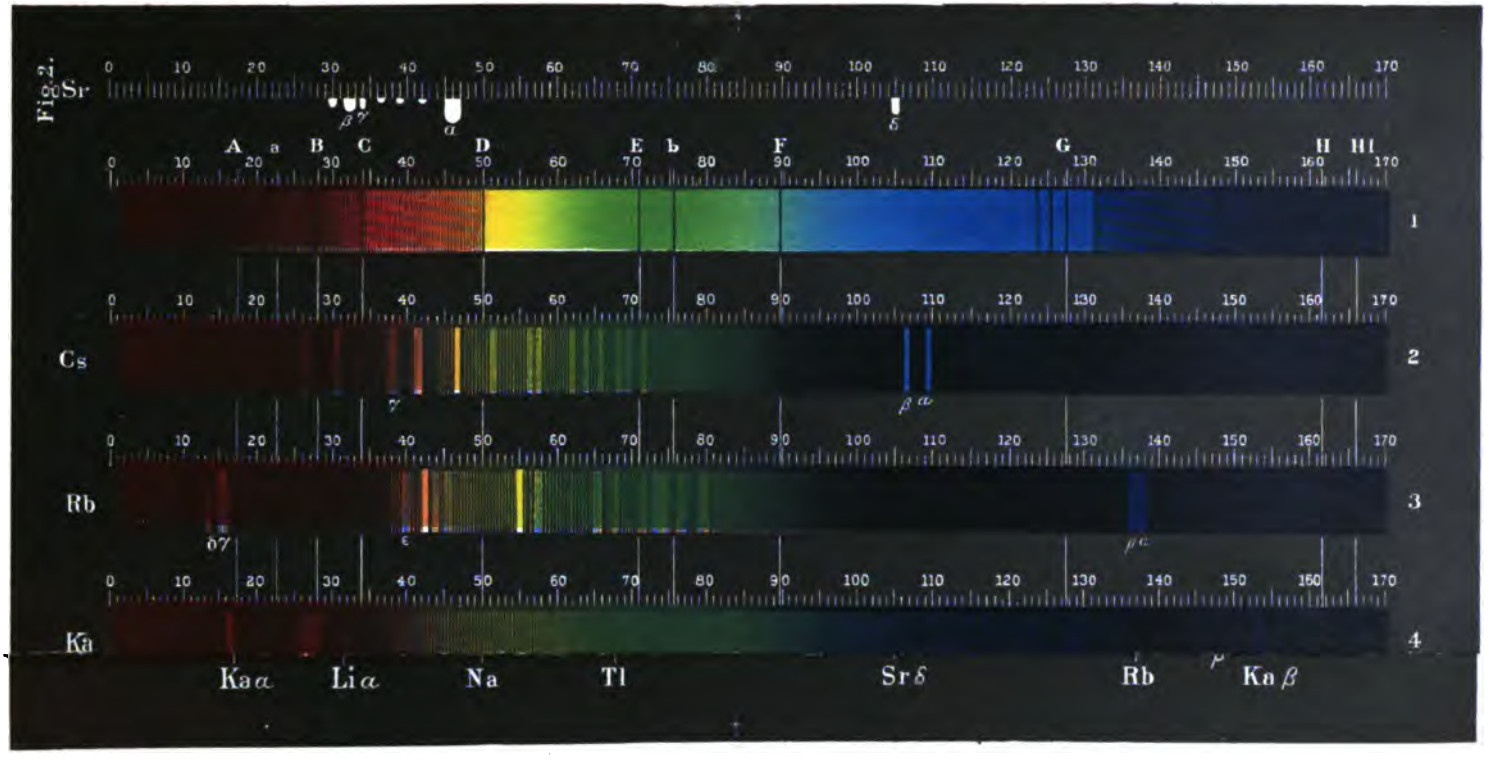
Fig. 21
Sr
A a B C D E b F G H H1
1
Cs
2
Rb
3
Ka
4
Ka α
Li α
Na
Tl
Sr δ
Rb
Ka β

MANUAL OF

QUALITATIVE CHEMICAL

ANALYSIS.

BY

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FIFTH EDITION.

NEW YORK:
JOHN WILEY & SONS, PUBLISHERS,
15 ASTOR PLACE.
1886.

Chem 668.86.3

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EDITOR'S PREFACE TO THE EDITION OF 1875.

THE matter of this new American edition of Fresenius' Manual of Qualitative Analysis, for the most part, faithfully represents the last (fourteenth) German edition. The editor has added a few paragraphs, has condensed, altered, or re-written some others, and has expunged the scheme for the "Analysis of Simple Compounds," after becoming convinced by experience that this omission not only greatly simplifies the analytical course, but really facilitates its mastery by the student.

A series of very brief analytical tables has been appended to this edition. These tables are borrowed, with some changes, from Mr. Vacher's English edition of 1869. No such tables, however elaborate, can take the place of Fresenius' systematic course, in the real work of the careful analyst, but they may be made very serviceable to the beginner in enabling him to survey his ground, as well as to the experienced chemist, when, being out of practice, he may need a brief outline of the order of operations to sharpen his memory.

In form the book is quite changed by the use throughout of the language and notation of "modern chemistry;" a change called for by the universal adoption of the "New System," as well as by its inherent advantages. For the convenience of the student, various developed formulæ are given on pages 49 and 50 and in numerous foot-notes. In these formulæ each dash, either horizontal, vertical or inclined, indicates a "bond" or unit of quantivalence, and implies chemical combination between the atoms or groupings whose symbols are thus connected. The + sign and period are used to express "molecular combination," *i.e.*, combination not amenable to the usually received quantivalences, as in case of crystal water.

EDITOR'S PREFACE TO THE EDITION OF 1883.

THE accidental destruction of the stereotype plates of the edition of 1875 having made a reprint necessary, the few typographical errors of the previous edition have been corrected, a few changes rendered necessary by the advance of knowledge have been made, instead of the plain spectrum map formerly given, a colored spectrum plate is supplied, and the print has been greatly improved and conformed to that of the last American edition of the Author's Quantitative Analysis. At the suggestion and with the advice of Professor O. D. Allen, all the reactions in Section III. which are not directly employed in the course of Analysis are printed in smaller type, as they may be advantageously passed over by the beginner. Several of the group recapitulations have been rearranged and simplified, and a few changes for the better made in the analytical scheme. Otherwise the work is essentially unaltered, and in its present form the editor confidently believes it to excel in convenience of use to teacher and pupil as it long has stood first in fulness and accuracy of statement.

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PART I.

INTRODUCTORY.

PRELIMINARY REMARKS.

ANALYTICAL chemistry is divided into two branches—viz., *qualitative analysis*, which studies the *nature* and properties of the component parts of bodies; and *quantitative analysis*, which ascertains the *quantity* of every individual element present. The office of qualitative analysis is to exhibit the constituent parts of a substance of *unknown* composition in forms of *known* composition, from which the constitution of the body examined, and the presence of its several component elements, may be positively inferred. The efficiency of its method depends upon two conditions—viz., it must attain the object in view with unerring certainty, and in the most expeditious manner. The object of quantitative analysis, on the other hand, is to exhibit the elements revealed by the qualitative investigation in forms which will permit the most accurate estimate of their weight, or to effect by other means the determination of their quantity.

The study of qualitative analysis must be pursued separately from that of quantitative analysis, and must naturally precede it.

For a successful pursuit of qualitative investigations, it is absolutely indispensable that the student should possess some knowledge of the chemical *elements*, and of their most important combinations, as well as of the principles of chemistry in general; and that he should combine with this knowledge some readiness in the apprehension of chemical processes. The practical part of this science demands, moreover, strict order, great neatness, and a certain skill in manipulation. If the student joins to these qualifications the

habit of invariably ascribing the failures with which he may happen to meet to some error or defect in his operations, or, in other words, to the absence of some condition indispensable to the success of the experiment—and a firm reliance on the immutability of the laws of nature cannot fail to create this habit—he possesses every requisite to render his study of analytical chemistry successful.

Although chemical analysis is based on general chemistry, and cannot be cultivated without some knowledge of the latter, yet, on the other hand, we have to look upon it as one of the main pillars upon which the entire structure of the science rests; since it is of almost equal importance for all branches of theoretical as well as of practical chemistry.

This consideration would be sufficient reason to recommend a thorough study of this branch of science, even if its cultivation lacked those attractions which it possesses for every one who devotes himself ardently to it. The mind is constantly striving for the attainment of truth; it delights in the solution of problems; and where do we meet with a greater variety of them, more or less difficult of solution, than in the province of chemistry? but as a problem to which, after long pondering, we fail to discover the key, wearies and discourages the mind, so do chemical investigations, if the object in view be not attained—if the results do not bear the stamp of unerring certainty. A *half-knowledge* is, therefore to be considered worse than no knowledge at all; and a *superficial* cultivation of chemical analysis is to be particularly guarded against.

A qualitative investigation may be made with a twofold view—viz., either, 1st, to prove that a certain body is or is not contained in a substance, *e.g.* lead in wine; or, 2d, to ascertain *all* the constituents of a chemical compound or mixture. Any substance whatever may of course become the object of a chemical analysis.

In this work those bodies which are most important in practical chemistry, from their wide distribution and their uses in medicine and the arts, are treated of in full detail; while, to facilitate the beginner's progress, the rarer elements are noticed more briefly, and in such a manner that they may be separately studied.

The study of qualitative analysis is most properly divided into four principal parts—viz.:

1. CHEMICAL OPERATIONS.
2. REAGENTS AND THEIR USES.
3. DEPORTMENT OF THE VARIOUS BODIES WITH REAGENTS.
4. SYSTEMATIC COURSE OF QUALITATIVE ANALYSIS.

It will be readily understood that the pursuit of chemical analysis requires *practical skill and ability*, as well as *theoretical knowledge;* and that mere speculative study can as little lead to success as purely empirical experiments. To attain the desired end, theory and practice must be judiciously combined.

SECTION I.

OPERATIONS.

§ 1.

THE operations of analytical chemistry are essentially the same as those of synthetical chemistry, though modified to a certain extent to adapt them to the different object in view, and to the small quantities operated upon in analytical investigations.

The following are the principal operations in qualitative analysis:

§ 2.

1. SOLUTION.

The term "*solution*," in its widest sense, denotes the union of a body, whether gaseous, liquid, or solid, with a fluid, resulting in a homogeneous liquid. When the substance dissolved is *gaseous*, the term "*absorption*" is more properly made use of; and the solution of one fluid in another is more generally called a *mixture*. The term solution, in its more usual sense, means the union of a *solid* body with a liquid.

A solution is the more readily effected the more minutely the body to be dissolved is divided. The fluid by means of which the solution is effected is the *solvent*. We call the solution *chemical*, where the solvent enters into chemical combination with the substance dissolved; *simple*, where no definite combination takes place.

In a *simple* solution the dissolved body is supposed to exist in the free state, and to retain all its original properties, except those dependent on its form and cohesion; since it separates unaltered when the solvent is withdrawn. Common salt dissolved in water is a familiar instance of a simple solution. The salt imparts its peculiar taste to the liquid. On evaporating the water, the salt is left behind in its original form. A simple solution is called *saturated* when the solvent contains all it can hold of the dissolved substance. But as

fluids generally dissolve larger quantities of a substance the higher their temperature, the term *saturated*, as applied to *simple* solutions, is only relative, and refers invariably to a certain temperature. As a general rule, elevation of temperature facilitates and accelerates simple solution. This rule has but few exceptions.

A *chemical* solution contains the dissolved substance not in the same state nor possessed of the same properties as before; the dissolved body is intimately combined with the solvent, which latter also has lost its original properties; a new substance has thus been produced, and the solution, therefore, manifests the properties of this new substance. A chemical solution also may be usually *accelerated* by elevation of temperature, since heat generally promotes the action of bodies upon each other. But the *quantity* of the dissolved body remains always the same in proportion to a given quantity of the solvent, the combining proportions of substances being invariable, and independent of the gradations of temperature.

The reason of this is, that in a chemical solution the solvent and the body upon which it acts have, more or less, opposite properties, which tend to neutralize each other. Solution ceases as soon as this tendency is satisfied. The solution is in this case also said to be saturated, or, more properly, *neutralized*, and the point which denotes it to be so is termed the point of saturation or neutralization.

The substances which produce chemical solutions are, in most cases, either acids or alkalies. With few exceptions, they have first to be converted to the fluid state by means of a simple solvent. When the opposite properties of acid and base are mutually neutralized, and the new compound is formed, the actual transition to the fluid state will ensue only if the new compound possesses the property of forming a simple solution with the liquid present; *e.g.* when solution of acetic acid in water is brought into contact with lead oxide there ensues, first, a chemical combination between the acid and the oxide, and then a simple solution of the new-formed lead acetate in the water present.

In pharmacy, solutions are often made in a mortar by triturating the body to be dissolved with the solvent added gradually in small quantities at a time; in chemical labora-

tories solutions are rarely made in this manner, but generally by digesting or heating the substance to be dissolved with the fluid in beaker-glasses, flasks, test-tubes, or capsules. In the preparation of chemical solutions, the best way generally is to mix the body to be dissolved in the first place with water (or with whatever other indifferent fluid may happen to be used), and then gradually add the chemical agent. By this course of proceeding a large excess of the latter is avoided, an over-energetic action guarded against, the process greatly facilitated, and complete solution insured, which is a matter of some importance, as it will not seldom happen in chemical combinations that the product formed refuses to dissolve if an excess of the chemical solvent is present; in which case the molecules first formed of the new salt, being insoluble in the menstruum present, gather round and enclose the portion still unacted on, weakening thereby or preventing altogether further chemical action upon them. Thus, for instance, witherite (barium carbonate) dissolves readily when, after being reduced to powder, water is poured upon it, and hydrochloric acid gradually added; but it dissolves with difficulty and imperfectly when projected into a concentrated solution of hydrochloric acid in water, for barium chloride will indeed dissolve in water, but not in hydrochloric acid.

CRYSTALLIZATION and PRECIPITATION are the reverse of solution, since they have for their object the conversion of a fluid or dissolved substance to the solid state. As both generally depend on the same cause, viz., on the absence of a solvent, it is impossible to assign exact limits to either; in many cases they merge into one another. We must, however, consider them separately here, as they differ essentially in their extreme forms, and as the special objects which we purpose to attain by their application are generally very different.

§ 3.

2. CRYSTALLIZATION.

We understand by the term crystallization, in a more

general sense, every operation, or process, whereby bodies are made to pass from the fluid to the solid state, and to assume certain fixed, mathematically definable, regular forms. But as these forms, which we call *crystals*, are usually the more regular, and consequently the more perfect, the more slowly the operation is carried on, we commonly connect with the term "crystallization" the accessory idea of a *slow* separation —of a *gradual* conversion to the solid state. The formation of crystals depends on the regular arrangement of the constituent particles of bodies (*molecules*); it can only take place, therefore, if these molecules possess perfect freedom of motion, and thus, in general, only when a substance passes from the fluid or gaseous to the solid state. Those instances in which the mere ignition, or the softening or moistening of a solid body, suffices to make the tendency of the molecules to a regular arrangement (crystallization) prevail over the diminished force of cohesion—such as, for instance, the turning white and opaque of moistened barley-sugar—are to be regarded as exceptional cases.

To induce crystallization, the causes of the fluid or gaseous form of a substance must be removed. These causes are either *heat alone, e.g.*, in the case of fused metals; or *solvents alone*, as in the case of an aqueous solution of common salt; or *both combined*, as in the case of a hot saturated solution of potassium nitrate in water. In the first case we obtain crystals by cooling the fused mass; in the second, by evaporating off the menstruum; and in the third, by either of these means. The most frequently occurring case is that of crystallization by cooling hot saturated solutions. The liquors which remain after the separation of the crystals are called *mother-liquors*. The term *amorphous* is applied to such solid bodies as have no crystalline form.

We have recourse to crystallization generally either to obtain the crystallized substance in a solid form, or to separate it from other substances dissolved in the same menstruum. In many cases also the form of the crystals or their deportment in the air, viz., whether they remain unaltered, or effloresce, or deliquesce, upon exposure to the air, will afford an excellent means of distinguishing between bodies otherwise resembling each other; for instance, between sodium sulphate and potassium sulphate. The process of crystal-

lization is usually effected in dishes, or, in the case of very small quantities, in watch-glasses, or finally in microscopic work, on slips or slides of thin plain glass.

Where the quantity of fluid to be operated upon is small, the surest way of getting well-formed crystals is to let the fluid evaporate in the air, or, better, under a bell-glass, over an open vessel half-filled with concentrated sulphuric acid. Minute crystals are examined best with a lens or microscope.

§ 4.

3. Precipitation.

This operation differs from the preceding one in that the dissolved body is *suddenly* converted to the solid state, no matter whether the substance separating is crystalline or amorphous, whether it sinks to the bottom of the vessel, or ascends, or remains suspended in the liquid. Precipitation is either caused by a modification of the solvent—thus calcium sulphate (gypsum) separates immediately from its solution in water upon the addition of alcohol; or it ensues in consequence of the separation of an *educt* insoluble in the menstruum—thus when ammonia is added to a solution of aluminium sulphate, the latter salt is decomposed, and aluminium hydroxide, not being soluble in water, precipitates. Precipitation takes place also when new compounds (*products*) are formed which are insoluble in the menstruum; thus calcium oxalate precipitates upon adding oxalic acid to a solution of calcium acetate; lead chromate, upon mixing potassium chromate with lead nitrate. In exchanges of this kind, one of the products remains generally in solution, and the same is sometimes the case also with the educt; thus, in the instances just mentioned, the ammonium sulphate, the acetic acid, and the potassium nitrate remain in solution. It may, however, happen also that both the product and the educt, or two products, precipitate, and that nothing remains in solution; this is the case, for instance, when a solution of magnesium sulphate is mixed with water of baryta, or when a solution of silver sulphate is precipitated with barium chloride.

Precipitation is resorted to for the same purposes as crystallization, viz., either to obtain a substance in the solid form,

or to separate it from other dissolved substances. But in qualitative analysis we have recourse to this operation more particularly for the purpose of detecting and distinguishing substances by the color, properties, and general deportment which they exhibit when precipitated either in an isolated state or in combination with other substances. The solid body separated by this process is called the *precipitate*, and the substance which acts as the immediate cause of the separation is termed the *precipitant*. Various terms are applied to precipitates by way of particularizing them according to their different nature; thus we distinguish crystalline, pulverulent, flocculent, curdy, gelatinous precipitates, etc.

The terms *turbid*, *turbidity*, or *cloudy* and *cloudiness*, are made use of to designate the state of a fluid which contains a precipitate so finely divided and so inconsiderable in amount, that the suspended particles, although impairing the transparency of the fluid, yet cannot be clearly distinguished. The separation of flocculent precipitates may generally be promoted by vigorous shaking; that of crystalline precipitates by stirring the fluid and rubbing the sides of the vessel with a glass rod; elevation of temperature is also an effective means of promoting the separation of most precipitates. The process is conducted, according to circumstances, either in test-tubes, flasks, or beakers.

The two operations described respectively in §§ 5 and 6, viz., FILTRATION and DECANTATION serve to effect the mechanical separation of fluids from matter suspended therein.

§ 5.

4. FILTRATION.

This operation consists simply in passing the fluid, from which we wish to remove the solid particles mechanically suspended therein, through a filtering apparatus formed usually by a properly arranged piece of unsized paper placed in a glass funnel; an apparatus of this description allows the fluid to trickle through, whilst it retains the solid particles. We employ *smooth filters* and *plaited filters;* the former in

cases where the separated solid substance is to be made use of, the latter in cases where it is wished to clear the solution rapidly.

[A smooth filter is prepared by folding a circular piece of filter paper first into halves, and then into quarters; then opening it out into a conical cup with three thicknesses on one side, and one on the other. In filtering, the filter should be opened, and pressed well down into the funnel so as to fit it closely.

Plaited filters are folded, as just described, into eighths, the folds all being made on *the same side* of the paper. Then each division is folded again upon itself on the *opposite side* of the paper; but to avoid breaking the latter, the folds should not reach quite to the centre. At this stage the filter has the appearance of a paper fan when shut. It is carefully opened out into a ribbed cone, pressed into the funnel, and evenly moistened from the vertex upwards, by aid of a gentle stream of water from the washing-bottle, Fig. 3.—EDITOR.]

In cases where the contents of the filter require washing, the paper must not project over the rim of the funnel. It is in most cases advisable to moisten the filter previously to passing the fluid through it; since this not only tends to accelerate the process, but also renders the solid particles less liable to be carried through the pores of the filter. The paper selected for filters must be as free as possible from inorganic substances, especially such as are dissolved by acids, *e.g.*, calcium and iron compounds.

FIG. 1.

The common filtering paper of commerce seldom comes up to our wants in this respect, and I would therefore always recommend to wash it carefully with dilute hydrochloric acid whenever it is intended for use in *accurate analyses*. For this purpose the apparatus shown in Fig. 1 will be found convenient. A is a bottle with the bottom out: *a* and *b* are glass plates: between them lie the filters, which have been previously cut and folded; *d* is a glass tube fitted into the cork *c*; *e* is a piece of flexible tube, which is closed by a piece of glass rod or a clip. The bottle is filled with a mixture of one part hydrochloric acid sp. gr. 1.12 and two

parts water, in which the filters are allowed to soak twelve hours, the acid being then run off and replaced by ordinary water. After an hour this is replaced by fresh water, and so on till the washings are barely acid. The washing is continued with distilled water till the washings are free from hydrochloric acid —that is, till they cease to give any turbidity when mixed with a few drops of solution of silver nitrate. Finally, the filters are drained, turned out upon blotting paper, covered with the same, and dried in a sieve in a warm place. When we merely want to wash two or three filters, we place them in a funnel as in filtering, one inside the other, moisten them with dilute hydrochloric or nitric acid, and after some time wash them well with distilled water.

Filtering paper, to be considered good, must, besides being pure, also let fluids pass readily through, whilst yet completely retaining even the finest pulverulent precipitates, such as barium sulphate, calcium oxalate, etc. If a paper satisfying these requirements cannot be readily procured, it is advisable to keep two sorts, one of greater density for the separation of very finely divided precipitates, and one of greater porosity for the speedy separation of grosser particles. The stand shown in Fig. 2 is adapted for supporting the small sized funnels used in qualitative analyses. Funnels are also often sustained in the mouths of flasks, test-tubes, or narrow beakers.

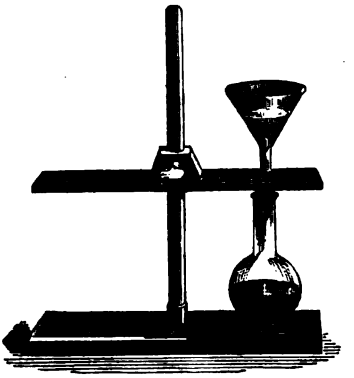


FIG. 2.

[*Rapid Filtration*, as made practical by BUNSEN, is described in the American Edition of Fresenius' Quantitative Analysis, pp. 91–98.

When hydrant water under high pressure is at hand, the most efficient and cheapest exhausting apparatus is the Jet Aspirator perfected by RICHARDS.]*

Filtration is greatly facilitated by prolonging the funnel-neck to a length of one foot by means of a glass tube of ½-inch bore and a short rubber connector. This glass tube should be contracted by fusion at its upper end to $\frac{1}{16}$-inch bore, so as to fill with the liquid.

§ 6.

5. DECANTATION.

This operation is frequently resorted to instead of filtration, in cases where the solid particles to be removed are of considerably greater specific gravity than the liquid in which they are suspended; as they will in such cases speedily subside to the bottom, thereby rendering it easy either to decant the supernatant fluid by simply inclining the vessel, or to draw it off by means of a syphon or a pipette.

* Am. Jour. Sci. [3] VIII. p. 412.

Certain slimy or gelatinous precipitates so clog the pores of paper as scarcely to admit of filtration. To obtain the liquid in which they have been formed quite clear, decantation is indispensable. Oftentimes the two processes may be advantageously combined by allowing the precipitate to settle as much as possible, and pouring off the still turbid liquid upon a filter.

§ 7.

6. Washing.

When filtration or decantation has been resorted to for the purpose of collecting a solid substance, the latter has to be freed afterward from the adhering liquid by repeated *washing* or *edulcoration*. The washing of precipitates collected on a filter is usually effected by means of a washing bottle, such as shown in Fig. 3.

This consists of a flask or bottle, closed with a twice-perforated, snugly-fitting rubber stopper, though which pass two glass tubes, as in the figure. The outer end of the tube, *a*, is drawn to a moderately fine point. By blowing into the other tube, a stream of water is driven out from *a* with considerable force, which adapts the apparatus to removing precipitates from the sides of vessels as well as to washing them on filters. This form of washing-bottle serves for edulcoration with warm or even boiling water, provided the vessel itself has a uniformly thin bottom, so that it can be heated without fear of breaking.

Fig. 3.

By binding about the neck a ring of cork, or winding it closely with smooth cord, it may be handled with convenience when its contents are hot. [By cutting the exit tube at *a*, and, after rounding their ends by fusion, uniting the two pieces with a bit of black rubber connector, the operator has it in his power to direct the outgoing stream upwards, or otherwise as he may desire, by applying the forefinger to the base of the movable portion. By a similar device, that part of the exit tube which enters the flask may be made flexible, so that the lower end shall remain immersed until all the water is expelled.—Ed.]

As the success of an analysis often depends upon the complete or proper washing of a precipitate, the operator must

accustom himself to continue the process patiently until he is certain that the object in view has been actually accomplished. In general, this is not the case until the precipitate has been perfectly freed from the liquor in which it was formed. The analyst must not be content to *guess* that a precipitate is thoroughly washed, but must *prove* that it is so, by applying appropriate tests, until experience enables him to know how long to continue the process in any given case. If the body to be removed is non-volatile, slow evaporation of a few drops of the last portions of the washings on a clean surface of glass or platinum will usually serve to indicate the point at which the process may terminate.

§ 8.

7. Dialysis.

Dialysis is an operation which may be employed for certain separations, and depends upon the different behavior of bodies dissolved in water towards moist membranes. Bodies that are able to crystallize (crystalloids, Graham) have the power of penetrating suitable membranes with which their solution may be placed in contact, whilst amorphous bodies, or colloids, viz., gum, gelatin, starch, albumen, silicic acid, etc., do not possess that property. Hence the two classes may be separated by taking advantage of this action. The septum must consist of a colloid material, as parchment paper, and it must on the other side be in contact with water. Figs. 4 and 5 exhibit suitable forms of apparatus for this operation. In Fig. 4, the dialyser consists of the top of a bottle closed below with parchment paper; in Fig. 5, it consists of a *gutta-percha* hoop covered like a sieve with parchment paper.

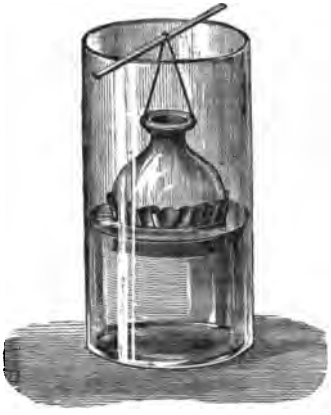


Fig 4.

The disk of parchment paper used should measure three or four inches in diameter more than the space to be covered; it is moistened, stretched over

and fastened by a string or by an elastic band, but it should not be secured too firmly. The parchment paper must not be porous ; its soundness may be tested by sponging the upper side with water, and observing whether wet spots show on the other side. Defects may be remedied by applying liquid albumen and coagulating this by heat.

[As MOHR suggests, the parchment paper may also be made into a plaited filter (§ 5), which, being supported in a funnel, is, with the latter, immersed in water contained in a beaker to the required depth.—ED.] When the dialyser has thus been got ready, the mass to be examined is poured into it. The depth of fluid in the dialysers above figured should not be more than half an inch, and the membrane should dip a little way below the surface of the water in the outer vessel, which should amount to at least four times the quantity of the fluid to be dialysed. [Mohr's dialyser may, of course, stand nearly its full depth in water.] After twenty-four hours, half or three-fourths of the crystalloids will be found in the external water, while the colloids remain in the dialyser—at most only traces pass into the external fluid. If the dialyser is brought successively in contact with fresh supplies of water, the whole of the crystalloids may be finally separated from the colloids. This operation is sometimes of service in chemico-legal investigations for the extraction of poisonous crystalloids from parts of a dead body, food, vomit, etc.

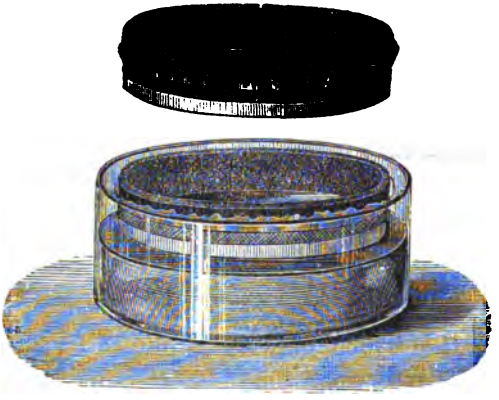


FIG. 5.

There are four operations which serve to separate volatile substances from less volatile or from fixed bodies, viz. EVAPORATION, DISTILLATION, IGNITION, and SUBLIMATION.

§ 9.

8. Evaporation.

This operation serves to separate volatile fluids from less volatile or from fixed bodies (solid or fluid) in cases where the residuary substance alone is of importance; thus we have recourse to evaporation for the purpose of removing from a saline solution part of the water, in order to bring about crystallization of the salt; also for removing the whole of the water from the solution of a non-crystallizable substance, so as to obtain the latter in a solid form, etc. The evaporated water is disregarded in these cases, the only object being to obtain in the one case a more concentrated fluid, and in the other a dry substance. These objects are attained by converting the fluid which is to be removed to the gaseous state. This is generally done by the application of heat; sometimes by leaving the fluid for a time in contact with the atmosphere, or with an enclosed volume of air kept dry by hygroscopic substances, such as concentrated sulphuric acid, calcium chloride, etc.; or, lastly, by placing the fluid in rarefied air, with simultaneous application of hygroscopic substances.

As it is of the utmost importance in qualitative analyses to guard against the least contamination, and as an evaporating fluid is the more liable to this the longer the operation lasts, the process is usually conducted with proper expedition, in porcelain or platinum dishes, over the flame of a spirit or gas lamp, in a place free from dust, preferably in a cupboard or hood provided with a draught. If the operator has no place of the kind, he must have recourse to covering the dish; the best way of doing this is to place over the dish a large glass funnel secured by a retort-holder, in a manner to leave sufficient space between the rim of the funnel and the border of the dish; the funnel is placed slightly aslant, that the drops running down its sides may be received in a beaker. Or the dish may also be covered with a sheet of filter paper previously freed from inorganic substances by washing with dilute hydrochloric or nitric acid (see § 5); were common and unwashed filter paper used for the purpose, the ferric oxide, lime, etc., contained in it would dissolve in the vapors evolved (more especially if acid), and the solution dripping down into the evaporating fluid would speedily contaminate it. These precautions are necessary, of course, only in accurate analyses. Large quantities of fluid are evaporated best in flasks standing aslant, covered with a cap of pure filtering paper, over a charcoal fire or gas; or also in tubulated retorts with neck rising obliquely upward, and open tubulure. Evapo-

Fig. 6.

rating processes at 100° are conducted in a suitable steam apparatus, or on the water-bath shown in Fig. 6. Evaporation to dryness is not usually conducted over the naked flame, but generally either on the water-bath or the sand-bath, or on an iron plate.

It should be remembered that porcelain and glass vessels—which we can hardly avoid using for the evaporation of large quantities of fluids—are always somewhat acted upon so that their contents become more or less contaminated. This action is but slight in case of most dilute acids or acid liquids, but the student should never evaporate *alkaline fluids* in glass, as at a boiling temperature they attack it considerably.

§ 10.

9. Distillation.

This operation serves to separate a volatile liquid from a less volatile or a non-volatile substance, where the object is to recover the evaporating fluid. A distilling apparatus consists of three parts: 1st, a vessel in which the liquid to be distilled is heated, and thus converted into vapor; 2d, an

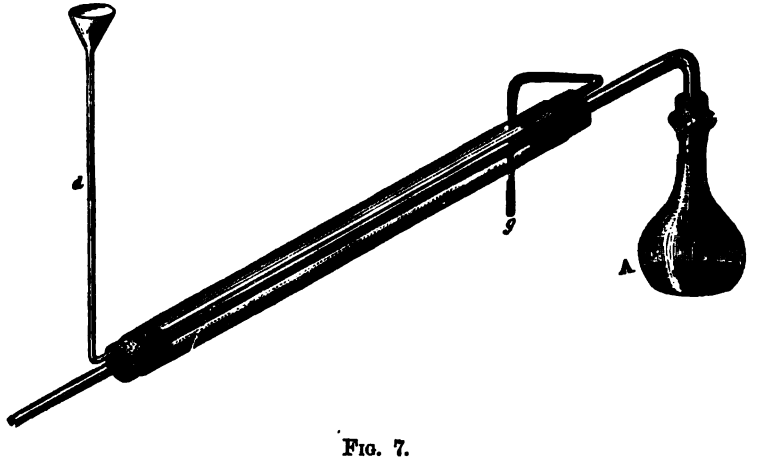


Fig. 7.

apparatus in which this vapor is cooled again or condensed, and thus reconverted to the fluid state; and 3d, a vessel to receive the fluid thus reproduced by the condensation of the vapor (the distillate). For the distillation of large quantities metallic apparatus are used (copper stills with head and con-

denser of tin), or large glass retorts; in analytical investigations we either use small retorts with receivers, or more usually an apparatus such as is shown in Fig. 7. The fluid to be distilled is boiled in A, and the vapor escapes through the tube which is fitted into the cork. The tube is surrounded with a wider tube which is filled with cold water, and is renewed continually or occasionally by pouring in through *d*, after placing a vessel under *g* to catch the hot water which will run out. A small flask serves as a receiver.

§ 11.

10. Ignition.

Ignition is, in a certain sense, for solid bodies what evaporation is to fluids; since it serves (at least generally) to separate volatile substances from less volatile or from fixed bodies, in cases where the residuary substance alone is of importance.

In some instances, substances are ignited simply for the purpose of modifying their state, without any volatilization taking place; thus chromic oxide is converted by ignition into the insoluble modification, etc. Substances are often ignited also, that the operator may from their deportment at a red heat draw a conclusion as to their nature in general, their fixity, their fusibility, the presence or absence of organic matter, etc.

Crucibles are the vessels generally made use of in ignition. In operations on a large scale, Hessian or black-lead crucibles are used, heated by charcoal or gas; in analytical experiments small-sized crucibles or dishes are selected, of porcelain, platinum, silver, or iron, or glass tubes sealed at one end, according to the nature of the substances to be ignited; these crucibles, dishes, or tubes are heated over a spirit or gas lamp, or a bellows blowpipe.

§ 12.

11. Sublimation.

The term *sublimation* designates the process which serves to

convert solid bodies into vapor by the application of heat, and subsequently to recondense the vapor to the solid state by refrigeration ;—the substance volatilized and recondensed is called a *sublimate*. Sublimation is consequently a *distillation of solid bodies*. We have recourse to this process mostly to effect the separation of substances possessed of different degrees of v. latility. In sublimations for analytical purposes we generally employ sealed glass tubes. When the sublimation is performed with the aid of a current of hydrogen or carbon dioxide we use open glass tubes, which are usually made narrower just behind the part to which the heat is applied.

§ 13.

12. Fusion and Fluxing.

Simple fusion is the conversion of a solid substance into the fluid form by the application of heat; it is most frequently resorted to for the purpose of effecting the combination or the decomposition of bodies. The term is also applied in cases where substances insoluble or difficult of solution in water and acids are by fusion in conjunction with some other body modified, decomposed, or fluxed in such a manner that they or the new-formed compounds will subsequently dissolve in water or acids. Fusion is conducted either in porcelain, silver, or platinum crucibles. The crucible is supported on a triangle of moderately stout platinum wire, resting on, or attached to, the iron ring of the spirit or gas lamp. Triangles of thick iron wire, especially when laid upon the stouter brass ring of the lamp, carry off too much heat to allow of the production of very high temperatures. Small quantities of matter are also often fused in glass tubes sealed at one end.

Resort to fusion is especially required for the analysis of various insoluble sulphates, silicates, and aluminium compounds. The flux most commonly used is sodium carbonate. In certain cases a mixture of calcium carbonate and ammonium chloride is employed.

For the fusion of aluminates, sodium disulphate is frequently used.

A platinum crucible is used for the fusion in all these cases just named.

Precautionary rules for the prevention of damage to platinum vessels.—No substance evolving chlorine ought to be treated in platinum vessels; no sodium or potassium nitrate or hydroxide or cyanide, no metals or sulphides of metals, should be fused in such vessels; nor should readily deoxidizable metallic oxides or organic salts of the heavy metals be ignited in them, or phosphates in presence of organic compounds. It is also detrimental to platinum crucibles, and especially to their covers, to expose them direct to an intense charcoal fire, as the action of the ash is likely to lead to the formation of platinum silicide, which renders the vessel brittle. It is always advisable to support platinum crucibles used in ignition or fusion on triangles of platinum wire. When a platinum crucible has been made white hot over the bellows blowpipe, it is unwise to cool it too quickly by suddenly turning off the gas, and allowing the cold blast to play upon it, since the crucible is under these circumstances very liable to become slightly cracked.

[When platinum vessels are ignited in the inner blue gas flame, they are liable to assume a dull and soiled aspect externally and after prolonged use often become cracked with rifts, that at first are scarcely perceptible, but shortly extend so as to ruin the vessel. This detriment is prevented, and generally most kinds of stains may be removed from platinum apparatus by gently rubbing the surface with wet sea-sand as often as the lustre is impaired. The grains of sand must be polished and free from sharp angles. By the proper use of sand of good quality, the metal is not scoured, but *burnished*.—Ed.] If the stains or impurities in a platinum dish resist this treatment, sodium disulphate or borax should be heated in it to fusion for some time. The vessel is then cleaned with hot water, and finally, if needful, is burnished with sand as above described.

§ 14.

13. Deflagration.

We understand by the term *deflagration*, in a more general sense, every process of decomposition attended with noise or detonation. We use the same term, however, in a more restricted sense, to designate the oxidation of a substance in the dry way, at the expense of the oxygen of another substance mixed with it (usually as a nitrate or a chlorate), and connect with it the idea of a sudden combustion attended with incandescence and detonation.

Deflagration is resorted to either to produce a desired body—thus arsenious sulphide is deflagrated with potassium nitrate to obtain potassium arsenate; or it is applied as a means to prove the presence or absence of a certain substance—thus salts are tested for nitric or chloric acid by fusing them with potassium cyanide, and observing whether they deflagrate, etc. To attain the former object, the perfectly

dry mixture of the substance and the deflagrating agent is projected in small portions at a time into a red-hot crucible. Experiments of the latter description are invariably made with minute quantities, preferably on a piece of thin platinum foil, or in a small spoon.

§ 15.

14. The Use of the Blowpipe.*

This operation is of paramount importance in many analytical processes. We have to examine here the apparatus required, the mode of its application, and the results of the operation.

The blowpipe, Fig. 8, is a small instrument, usually made of brass or German silver. It consists of three parts, viz., 1st, a tube, *a b*, fitted, for greater convenience, with a horn or ivory mouthpiece, through which air is blown from the mouth; 2d, a small cylindrical vessel, *c d*, into which *a b* is screwed air-tight, and which serves as an air-chamber and to retain the moisture of the air blown into the tube; and 3d, a smaller tube, *f g*, also fitted into *c d*. This small tube, which forms a right angle with the larger one, is fitted at its aperture either simply with a finely perforated platinum plate, or more conveniently with a finely perforated platinum cap *(h)*. The construction of the cap is shown in Fig. 9. It is, indeed, a little dearer than a simple plate, but it is also much more durable. If the opening of the cap gets stopped up, the obstruction may generally be removed by heating it to redness before the blowpipe.

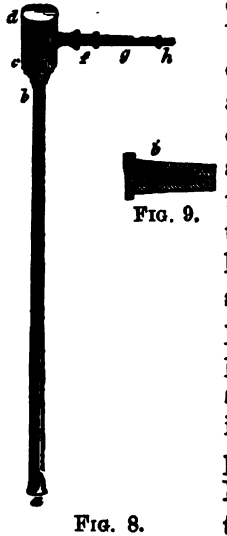


Fig. 9.

Fig. 8.

The proper length of the blowpipe depends upon the distance to which the operator can see with distinctness; it is usually from eight so ten inches. The form of the mouthpiece varies. Some chemists like it of a shape to be encir-

* For fuller details of the use of the blowpipe, see Brush's Determinative Mineralogy.

cled by the lips; others prefer the form of a trumpet mouthpiece, which is only pressed against the lips. The latter requires less exertion on the part of the operator, and is accordingly generally chosen by those who have a great deal of blowpipe work.

Fig. 10.

The blowpipe serves to conduct a continuous fine current of air into a gas flame, or into the flame of a candle or lamp. The flame of a candle or lamp, burning under ordinary circumstances, is seen to consist of three principal parts, as shown in Fig. 10, viz., 1st, a dark nucleus in the centre (*a*); 2d, a luminous cone surrounding this nucleus (*e f g*); and 3d, a feebly luminous mantle encircling the whole flame (*b c d*). The dark nucleus contains the gases which the heat evolves from the wax or fat, and which cannot burn here for want of oxygen. In the luminous cone these gases come in contact with a certain amount of air insufficient for their complete combustion. In this part, therefore, it is principally the hydrogen of the hydrocarbons evolved which burns, whilst the carbon separates in a state of intense ignition, which imparts to the flame the luminous appearance observed in this cone. In the outer coat the access of air is no longer limited, and all the matter not yet burned is consumed here. This part of the flame is the hottest, and the extreme apex is the hottest point of it. Oxidizable bodies oxidize, therefore, with the greatest possible rapidity when placed in it, since all the conditions of oxidation are here united, viz., high temperature and an unlimited supply of oxygen. This outer part of the flame is therefore called the *oxidizing flame.*

On the other hand, oxides having a tendency to yield up their oxygen suffer *reduction* when placed within the luminous part of the flame, the oxygen being withdrawn from them by the carbon and the still unconsumed hydrocarbons there present. The luminous part of the flame is therefore called the *reducing flame.*

The effect of blowing a fine stream of air across a flame is, first, to alter the shape of the flame, as, from tending upward, it is now driven sideways in the direction of the blast, being at the same time lengthened and narrowed; and, in the second place, to extend the sphere of combustion from the

outer to the inner part. As the latter circumstance causes an extraordinary increase in the heat of the flame, and the former a concentration of that heat within narrower limits, it is easy to understand the exceedingly energetic action of the blowpipe flame. The way of holding the blowpipe and the nature of the blast will depend upon whether the operator wants a reducing or an oxidizing flame. The easiest way of producing most efficient flames of both kinds is by means of coal-gas delivered from a jet, shaped as in Fig. 11, the slit

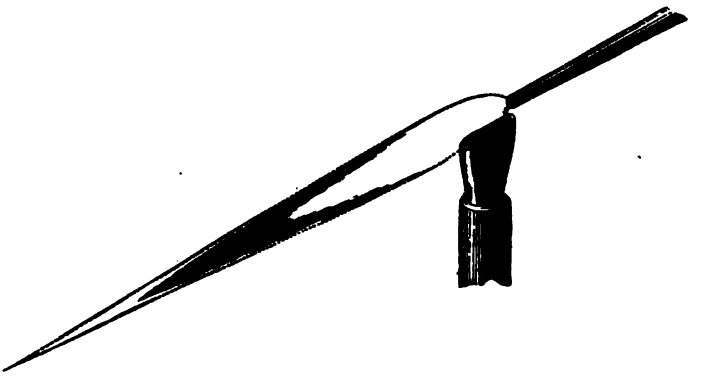


Fig. 11.

being 1 centimetre long, and 1½ to 2 millimetres wide; as with the use of gas the operator is enabled to regulate not only the current of air, but that of the gas also. The task of keeping the blowpipe steadily in the proper position may be greatly facilitated by firmly resting that instrument upon some movable metallic support, such as, for instance, the ring of Bunsen's gas-lamp intended for supporting dishes, etc.

Fig. 11 shows the flame for reducing; Fig. 12 the flame for oxidizing. The luminous parts are shaded.

The *reducing flame* is produced by keeping the jet of the blowpipe just on the border of a tolerably strong gas flame, and driving a moderate blast across it. The resulting mixture of the air with the gas is only imperfect, and there remains between the inner bluish part of the flame and the outer barely visible part a luminous and reducing zone, of which the hottest point lies somewhat beyond the apex of the inner cone. To produce the *oxidizing flame*, the gas is lowered, the

jet of the blowpipe pushed a little farther into the flame, and the strength of the current somewhat increased. This serves to effect an intimate mixture of the air and gas, and an inner pointed, bluish cone, slightly luminous towards the apex, is formed, and surrounded by a thin, pointed, light-bluish, barely visible mantle. The hottest part of the flame is at the apex

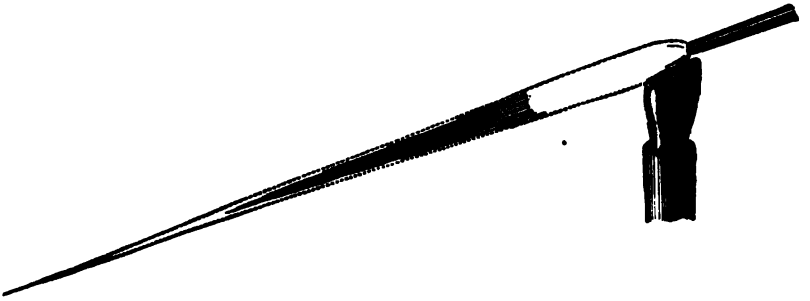


FIG. 12.

of the inner cone. Difficultly fusible bodies are exposed to this part to effect their fusion; but bodies to be oxidized are held a little beyond the apex, that there may be no want of air for their combustion. An oil-lamp with broad wick of proper thickness may be used instead of gas; a thick wax-candle also will do. For an oxidizing flame a small spirit-lamp will in most cases answer the purpose.

The *current* is produced with the cheek muscles alone, and not with the lungs. The way of doing this may be easily acquired by practising for some time to breathe quietly with distended cheeks and with the blowpipe between the lips; with practice and patience the student will soon be able to produce an even and uninterrupted current.

The *supports* on which substances are exposed to the blowpipe flame are generally either wood charcoal, or platinum wire or foil.

Charcoal supports are used principally in the reduction of metallic oxides, etc., or in trying the fusibility of bodies. The substances to be operated upon are put into small cavities, scooped out with a penknife or with a little tin tube. Metals that are volatile at the heat of the reducing flame evaporate wholly or in part upon the reduction of their oxides; in passing through the outer flame the metallic fumes are re-

oxidized, and the oxide formed is deposited around the portion of matter upon the support. Such deposits are called incrustations. Many of these exhibit characteristic colors, leading to the detection of the metals. The charcoal of pine, linden, or willow is greatly preferable to that of harder woods. Saw the thoroughly burnt charcoal of well-seasoned and straight-split pine wood into rectangular pieces, and brush off the dust; they may then be handled without soiling the hands. Those sides alone are used on which the annual rings are visible on the edge, as on the other sides the fused matters are apt to spread over the surface of the charcoal. Small charcoal supports are sometimes sold, which have been made from powdered charcoal, mixed with rice or starch paste, and stamped into convenient shapes—they are very handy and clean.

Charcoal is so valuable a material for supports in blowpipe experiments because of—1st, its infusibility; 2d, its low conducting power for heat, which permits substances being heated more strongly upon a charcoal than upon any other support; 3d, its porosity, which makes it imbibe readily fusible substances, such as borax, sodium carbonate, etc., whilst infusible bodies remain on the surface; 4th, its reducing power, which greatly contributes to the reduction of oxides in the inner blowpipe flame.

We use *platinum wire*, and occasionally also *platinum foil*, in all oxidizing processes before the blowpipe, and also when fusing substances with fluxes, with a view to try their solubility in them, and to watch the phenomena attending the solution, and mark the color of the bead; lastly, also to introduce substances into the flame, to see whether they will color it. The wire is cut into lengths of 8 centimetres, and each length

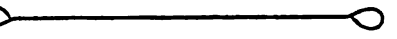


Fig. 13.

twisted at both ends into a small loop (Fig. 13). When required for use, the loop is moistened with a drop of water, then dipped into the powdered flux (where a flux is used), and the portion adhering fused in the flame of a gas or spirit lamp. When the bead produced, which sticks to the loop, is cold, it is moistened again, and a small portion of the sub-

stance to be examined put on and made to adhere to it by the action of a gentle heat. The loop is then finally exposed, according to circumstances, to the inner or the outer blowpipe flame.

What renders the application of the blowpipe particularly useful is the great expedition with which results are attained. These results are of a two-fold kind, viz., either they afford us simply an insight into the general properties of the body, and enable us accordingly only to determine whether it is fixed, volatile, fusible, etc.; or the phenomena which we observe enable us at once to recognize the particular body which we have before us. We shall have occasion to describe these phenomena when treating of the deportment of the different substances with reagents.

Chemists have devised various forms of self-acting blowpipe apparatus, in some of which the air-current is produced by means of a gasometer, in others by means of a caoutchouc balloon, in others again by a species of hydrostatic blast, etc. But the simplest self-acting apparatus, by which most of the objects attainable with the blowpipe may be conveniently accomplished, is the Bunsen gas-lamp, provided with a chimney, which burns without luminosity and without soot. A description of this lamp follows in the next paragraph.

§ 16.

15. The Use of Lamps, particularly of Gas-lamps.

As we have to deal mostly with small quantities of matter, we commonly use in processes of qualitative analysis requiring the application of heat, such as evaporation, ignition, etc., either spirit-lamps or gas-lamps.

Of *spirit-lamps* there are two kinds in use, viz., the simple spirit-lamp, as shown in Fig. 16, and the Berzelius lamp with double draught (Fig. 14). In the construction of the latter lamp it should be borne in mind that the part containing the wick and the vessel with the spirit must be in separate pieces connected only by means of a narrow tube; otherwise troublesome explosions are apt to occur in lighting the lamp. Nor should the chimney be too narrow, or the stopper fit air-tight on the mouth through which the spirit is poured in. A lamp

should be selected that may be readily moved up and down the pillar of the stand, which must be fitted with a movable brass ring to support dishes and flasks in processes of ebullition, and a ring of moderately stout iron wire to support the triangle for holding the crucibles in the processes of ignition and fusion. Of the various forms of lamps in use, the one shown in Fig. 14 is the most suitable. Fig. 15 shows a triangle of platinum wire fixed within an iron-wire triangle: this serves to support the crucible in processes

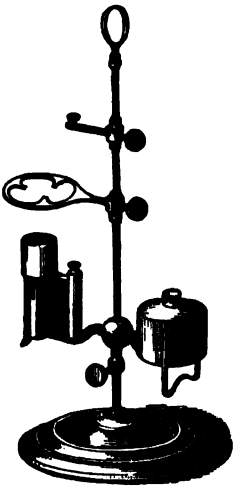


Fig. 14.

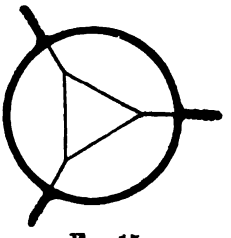


Fig. 15.

Fig. 16.

of ignition. Glass vessels, more particularly beakers, which it is intended to heat over the lamp, are most conveniently rested on a piece of gauze made of fine iron wire such as is used in making sieves of medium fineness.

Of the many *gas-lamps* proposed, Bunsen's, as shown in its simplest form in Figs. 17 and 18 is the most convenient. *a b* is a foot of cast iron. In the centre of this is fixed a brass box, *c d*, which has a cylindrical cavity of 12 mm. deep, and 10 mm. in diameter. Each side of the box has, 4 mm. from the upper rim, a circular aperture of 8 mm. diameter, leading to the inner cavity. One of the sides has fitted into it, 1 mm. below the circular aperture, a brass tube, which serves for the attachment of the India-rubber supply tube. This brass tube is turned in the shape shown in Fig. 17; it has a

bore of 4 mm. The gas conveyed into it re-issues from a tube in the centre of the cavity of the box. This tube, which is 4 mm. thick at the top, thicker at the lower end, projects 3 mm. above the rim of the box; the gas issues from a narrow opening which appears formed of 3 radii of a circle, inclined to each other at an angle of 120°. The length of each radius is 1 mm.; the opening of the slit is ½ mm. wide; *e f* is a brass tube 95 mm. long, open at both ends, with a bore of 9 mm.; the screw at the lower end of this tube fits into the upper part of the cavity of the box. With this tube screwed in, the

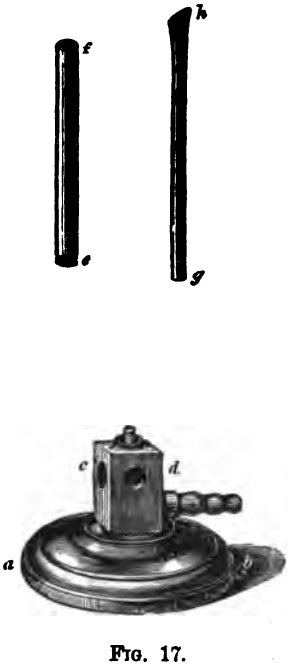


FIG. 17.

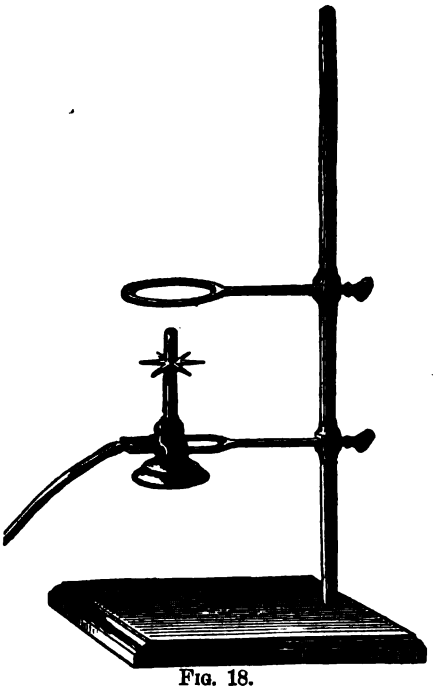


FIG. 18.

lamp is completed. On opening the stop-cock, the gas rushes into the tube *e f*, where it mixes with the air coming in through the circular apertures. When this mixture is kindled at *f*, it burns with a straight, upright, bluish flame, entirely free from soot, which may be regulated at will by opening the stop-cock more or less; a partial opening of the cock suffices to give a flame fully answering the purpose of the common spirit-lamp; whilst with the full stream of gas turned on, the flame,

which will now rise up to 2 decimetres in height, affords a most excellent substitute for the Berzelius lamp. If the flame is made to burn very low, it will often occur that it recedes; in other words, that instead of the mixture of gas and air burning at the mouth of the tube, *e f*, the gas takes fire on issuing from the slit, and burns below in the tube. This defect may be perfectly obviated by covering the tube, *e f*, at the top with a little wire-gauze cap. Flasks, etc., which it is intended to heat over the gas-lamp, are most conveniently supported on a *gauze plate*—a square piece of thin iron plate to which a piece of wire gauze of equal size is riveted, as shown in Fig. 19. Simple wire-gauze rapidly burns through in the middle, and does not offer the same protection against the cracking of beakers or flasks. For blowpipe operations, the tube *g h* must be inserted into *e f*; this tube terminates in a slanting flattened top, and having an opening in it 1 cm. long, 1½ to 2 mm. wide. The insertion of *g h* into *e f* serves to close the air-holes in the box, and pure gas, burning with a luminous flame, issues from the top of the tube. Fig. 18 shows the apparatus complete, fixed in the fork of an iron stand; this arrangement permits the lamp being moved backward and forward between the prongs of the fork, and up and down the pillar of the stand. The movable ring on the same pillar serves to support the objects to be operated upon. The 6 radii round the tube of the lamp serve to support an iron-plate chimney (see Fig. 23), or a porcelain plate used in quantitative analyses.

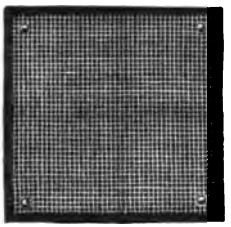


Fig. 19.

To heat crucibles to the brightest red heat, or to a white heat, the *bellows blowpipe* is resorted to. But even without this the action of the gas-lamp may be considerably heightened by heating the crucible within a small clay furnace, as recommended by Erdmann. Fig. 20 shows the simple contrivance by which this is effected. The furnaces are 115 mm. high, and measure 70 mm. diameter in the clear. The thickness of material is 8 mm. If the ordinary Bunsen burner is not suffi-

Fig. 20.

ciently strong for any purpose, the three-Bunsen burner (Fig 21) may be used.

BUNSEN has devised a more perfect form of this lamp* to render the flame a more complete substitute for the blowpipe flame, namely, for reducing, oxidizing, fusing, and volatilizing, and for the observation of the coloration of flame (§ 17). This improved form of the lamp is shown in Fig. 22. *a* is a sheath, which can be turned round for regulating the flow of air. When in use the conical chimney, *d d d d* (Fig. 23), is placed on *e e*; it is of such dimensions that the flame may burn tranquilly. Fig. 23 shows the flame half its natural size. In this three parts are at once apparent, namely, 1. *a a a a*, the dark cone, which contains the cold gas mixed with about 62 per cent. of air; 2. *a c a b*, the mantle formed by the burning mixture of gas and air; 3. *a b a*, the luminous tip of the

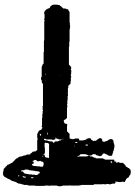


FIG. 21.

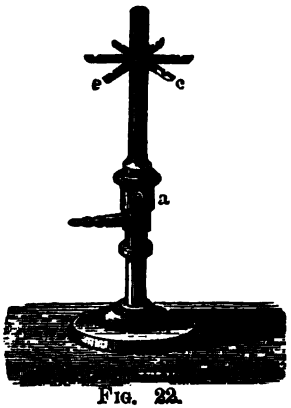


FIG. 22.

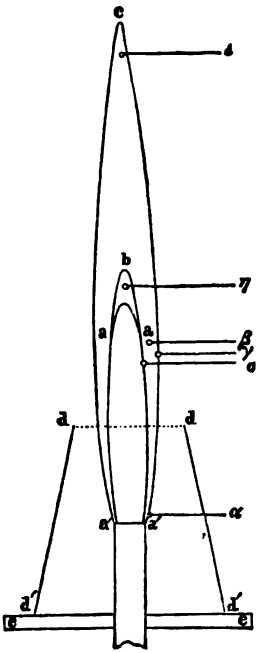


FIG. 23.

dark cone, which does not appear unless the air-holes are somewhat closed. The latter is useful for reductions.

* Annal. d. Chem. u. Pharm., 111, 257 and 138, 257. Also Zeitschr. f. anal. Chem., 5, 351.

Such are the three principal parts of the flame, but BUNSEN distinguishes no less than six parts, which he names as follows:

1. *The base* at α, which has a relatively low temperature, because the burning gas is here cooled by the constant current of fresh air, and also because the lamp itself conducts the heat away. This part of the flame serves for discovering the colors produced by readily volatile bodies when less volatile bodies which color the flame are also present. At the relatively low temperature of this part of the flame the former volatilize alone instantaneously, and the resulting color imparted to the flame is for a moment visible unmixed with other colors.

2. *The fusing zone.* This lies at β, at a distance from the bottom of somewhat more than one-third of the height of the flame, equidistant from the outside and the inside of the mantle, which is broadest at this part. This is the hottest part in the flame, namely, 2,300°, and it therefore serves for testing substances as to their fusibility, volatility, emission of light, and for all processes of fusion at a high temperature.

3. *The lower oxidizing flame* lies in the outer border of the fusing zone at γ, and is especially suitable for the oxidation of oxides dissolved in vitreous fluxes.

4. *The upper oxidizing zone* at ε consists of the non-luminous tip of the flame. Its action is strongest when the air-holes of the lamp are fully open. It is used for the roasting away of volatile products of oxidation, and generally for all processes of oxidation where the very highest temperature is not required.

5. *The lower reducing zone* lies at δ in the inner border of the fusing zone next to the dark cone. The reducing gases are here mixed with oxygen, and therefore do not possess their full power; hence they are without action on many substances which are deoxidized in the upper reducing flame. This part of the flame is especially suited for reduction on charcoal or in vitreous fluxes.

6. *The upper reducing flame* lies at η in the luminous tip of the dark inner cone, which, as I have already explained, may be produced by diminishing the supply of air. This part of the flame must not be allowed to get large enough to blacken a test-tube filled with water and held in it. It contains no free oxygen, is rich in separated incandescent carbon, and therefore has a much stronger action than the lower reducing zone.

It is used more particularly for the reduction of metals collected in the form of incrustations.

With the help of a gas flame of this description we can obtain as high a temperature as with the blowpipe, and even higher if the radiating surface of the substance is made as small as possible; and by the use of the different parts of the flame processes of reduction and of oxidation may be carried out with the greatest convenience.

In order to study *the deportment of bodies at a high temperature*, namely, their emission of light, fusibility, volatility, and power of coloring flame, they are introduced into the flame in the loop of a platinum wire, which should be barely thicker than a horse-hair. Should the substance attack platinum, a little bundle of asbestos is used, which should be about one-fourth the thickness of a match. Decrepitating substances are first very finely powdered, then placed on a strip of moistened filter paper about a square centimetre in surface, and this is cautiously burnt between two rings of fine platinum wire. The substance now presents the appearance of a coherent crust, and may be held in the flame without difficulty. For testing fluids to see whether they contain a substance which colors flame, the round loop of the fine platinum wire is flattened on an anvil to the form of a small ring. This is dipped into the fluid, and then withdrawn, when a drop will be found attached to the ring. This drop is held near the flame and allowed to evaporate without boiling, after which the residue may be conveniently tested.

If bodies are to be exposed for a considerable time to the action of the flame, the stand Fig. 24 is used. *A* and *B* are provided with springs, and can be easily moved up and down. On *A* is the arm *a*, intended for the support of the platinum wire fixed in the glass tube (Fig. 25); also another little arrangement to hold the glass tube *b*, with its bundle of asbestos fibres, *d*. *B* bears a clip for the reception of a test-tube, which in certain cases has to be heated for a considerable time in a definite part of the flame. *C* serves to hold the various platinum wires fixed in glass tubes.

Experiments of reduction are performed either with the aid of a suitable reducing agent in a small glass tube, or with the aid of a little stick of charcoal. In order to prepare the latter, BUNSEN recommends to hold an uneffloresced crys-

tal of sodium carbonate near the flame, and then having taken off the head of a match to smear three-fourths of its length with the wet mass produced by warming the crystal. The match-stick is then slowly rotated on its axis in the flame, when a crust of solid sodium carbonate will form on the carbonized wood, and on heating in the fusing zone of the flame this crust will be melted and absorbed by the charcoal. The little stick of charcoal will now in a measure be protected from combustion. The substance to be tested is made into a paste, with a drop of melted crystallized sodium carbonate, and a mass about the size of a millet-seed is taken up on the point of the carbonized match; it is then first melted in the lower oxidizing flame, and afterwards moved through a portion of the dark cone into the opposite hottest part of the lower reducing zone. The reduction will be rendered evident by the effervescence of the sodium carbonate. After a few moments the action is stopped by allowing the substance to cool in the dark cone of the flame. If, finally, the point of the carbonized match is cut off and triturated with a few drops of water in a small agate mortar, the reduced metal will be obtained in the form of sparkling fragments which may be purified by elutriation, and, if necessary, more minutely examined.

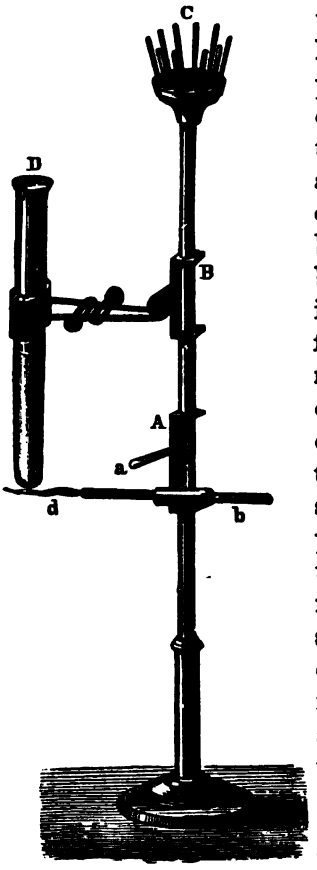


FIG. 24.

FIG. 25.

Volatile elements which are reducible by hydrogen and carbon may be separated as such or as oxides from their combinations and deposited on porcelain. These deposits are called *incrustations;* they are thicker in the middle, and be-

come thin towards the edges. They may be converted into iodides, sulphides, and other combinations, and may thus be further identified. These reactions are so delicate that in many cases a quantity of from $\frac{1}{10}$ to 1 mgrm. is sufficient to exhibit them.

The metallic incrustation is obtained by holding in one hand a small portion of the substance on asbestos in the upper reducing flame, and in the other a glazed porcelain dish, from 1 to 1.2 decimetres in diameter, filled with water, close over the asbestos in the upper reducing flame. The metals separate as sooty or mirror-like incrustations.

If the substance is held as just directed, and the porcelain dish is held in the upper oxidizing flame, then an *incrustation of oxide* is obtained. In order to be sure of getting it, the flame must be comparatively small if the portion of substance is minute. To turn the incrustation of oxide into an *incrustation of iodide*, let the dish covered with the oxide cool, breathe on it, and place it on the wide-mouthed bottle, Fig. 26. This bottle contains phosphorus tri-iodide, which has been allowed to deliquesce and become converted into fuming hydriodic acid and phosphorous acid; it should have an air-tight glass stopper. If the hydriodic acid has become so moist that it has ceased to fume, it may be restored to its proper condition by the addition of phosphoric pentoxide. To turn the incrustation of iodide into an *incrustation of sulphide*, direct a current of air containing ammonium sulphide upon it, breathing upon the dish occasionally; then drive off the excess of ammonium sulphide by *gentle* warming.

FIG. 26.

If more considerable quantities of the metallic incrustation are required for further experiments, the porcelain dish is replaced by a test-tube half filled with water, *D* (Fig. 24), in which a few pieces of marble should be placed to prevent bumping when the water subsequently boils. In this case the asbestos, *d*, with the substance on it, is fixed at the same height as the middle of the upper reducing flame, the test-tube is fixed with its bottom close over the asbestos, as shown in the figure, and then the lamp is moved just under

the test-tube. The substance thus comes within the reducing flame, and the metallic incrustation forms on the bottom of the test-tube. The incrustation may be obtained as thick as is wished by renewal of the substance.

§ 17.

16. Observation of the Coloration of Flame and Spectrum Analysis.

Many substances give characteristic tints to a colorless flame, which afford excellent means for their identification. Thus, for instance, salts of sodium impart to flame a yellow, salts of potassium a violet, salts of lithium a carmine tint, and may thus be easily distinguished from each other.

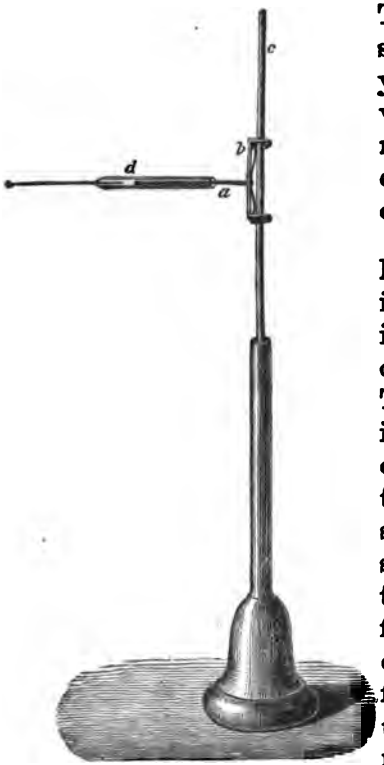


Fig. 27.

The flame of Bunsen's gas-lamp with chimney, described in § 16, and shown in Fig. 22, is more particularly suited for observations of this kind. The substances to be examined are put on the small loop of a fine platinum wire, and thus by means of the holder shown in Fig. 24, or the more simple one, Fig. 27, placed in the fusing zone of the gas flame. A particularly striking coloration is imparted to the flame by the volatile salts of the alkali and alkali-earth metals. If different salts of one and the same base are compared in this way, it is found that every one of them, if at all volatile at high temperatures, or permitting at least the volatilization of the base, imparts the same color to the flame,

only with different degrees of intensity, the most volatile of the salts producing also the most intense coloration; thus, for instance, potassium chloride gives a more intense coloration than potassium carbonate, and this latter again a more intense one than potassium silicate. In the case of difficultly volatile compounds, the coloration of the flame may often be developed by adding some other body which has the power of decomposing the compound under examination. Thus, for instance, in silicates containing only a few per cent. of potassium, the latter body cannot be directly detected by coloration of flame; but this detection may be accomplished by adding a little pure gypsum, as this will cause formation of calcium silicate and potassium sulphate, a salt which is sufficiently volatile.

But however decisive a test the mere coloration of flame affords for the detection of certain metallic compounds, when present unmixed with others, this test becomes apparently quite useless in the case of mixtures of compounds of several metals. Thus, for instance, mixtures of salts of potassium and sodium show only the sodium flame; mixtures of salts of barium and strontium, only the barium flame, etc. This defect may be remedied, however, in two ways.

The *first way*, introduced by CARTMELL,* and perfected afterwards by BUNSEN † and by MERZ,‡ consists in looking at the colored flame through some colored medium (colored glasses, indigo solution, etc.). Such colored media, in effacing the flame coloration of the one metal, bring out that of the other metal mixed with it. For instance, if a mixture of a salt of potassium and a salt of sodium is exposed to the flame, the latter will only show the yellow sodium coloration; but if the flame be now looked at through a deep-blue cobalt glass, or through solution of indigo, the yellow sodium coloration will disappear and will be replaced by the violet potassium tint. A simple apparatus suffices for all observations and experiments of the kind; all that is required for the purpose being—

1. A hollow prism (Fig. 28) composed of mirror-plates, the chief section of which forms a triangle with two sides of 150 mm., and one side of 35 mm. length. The indigo solution

* Phil. Mag. 16, 328. † Annal. d. Chem. u. Pharm., 111, 257.
‡ Journ. f. Prakt. Chem., 80, 487.

required to fill this prism is prepared by dissolving 1 part of indigo in 8 parts of fuming sulphuric acid, adding to the

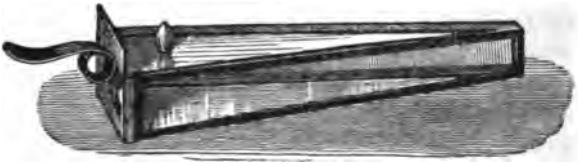


FIG. 28.

solution 1,500–2,000 parts of water, and filtering. When using this apparatus the prism is moved in a horizontal direction close before the eyes, in such a way that the rays of the flame are made to penetrate successively thicker and thicker layers of the effacing medium.

2. A blue, a violet, a red, and a green glass. The blue glass is tinted with cobalt monoxide; the violet glass with manganese sesquioxide; the red glass (white glass colored red superficially) with cuprous oxide; and the green glass with iron oxide and cupric oxide. The colored glass of commerce will generally be found to answer the purpose. As regards the tints imparted to the flame by the different bodies, when viewed through the aforesaid media, and the combinations by which these bodies are severally identified, the information required will be found in Section III., in the paragraphs treating of the several bases and acids.

The *second way*, which is called *Spectrum Analysis*, was introduced by KIRCHOFF and BUNSEN. It consists in letting the rays of the colored flame pass first through a narrow slit, then through a prism, and observing the so refracted rays through a telescope. A distinct spectrum is thus obtained for every flame-coloring metal; this spectrum consists either, as in the case of barium, of a number of colored lines lying side by side; or, as in the case of lithium, of two separate, differently colored lines; or, as in the case of thallium, of a single green line. These spectra are characteristic in a double sense—viz., the spectrum lines have a distinct color, and they occupy also a fixed position.

It is this latter circumstance which enables us to identify without difficulty, in the spectrum observation of mixtures of flame-coloring metals, every individual metal. Thus, for in-

stance, a flame in which a mixture of potassium, sodium, and lithium salts is evaporated, will give, side by side, the spectra of the several metals in the most perfect purity.

A spectroscope which suffices for all common purposes is shown in Fig. 29.

A is an iron disk, in the centre of which a prism, with circular refracting faces of about 25 mm. diameter, is fast-

Fig. 29.

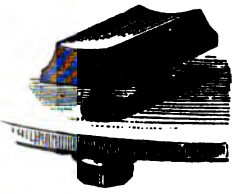


Fig. 29*a*.

ened by a clamp and screw. The same disk has also fastened to it the three tubes *B*, *C*, and *D*. Each of these tubes is soldered to a metal block (Fig. 29*a*), by which they may be adjusted in the proper position. *B* is the observation telescope; it has a magnifying power of about six. The tube *C* is closed at one end by a brass disk, into which the perpendicular slit is cut through which the light is admitted. The tube *D* carries a photographic copy of a millimetre scale, reduced on a glass plate to about one-fifteenth the original dimensions. This scale is covered with tin foil, with the exception of the narrow strip upon which the divisional lines and the numbers are engraved. It is lighted by a gas or candle flame placed before it.

The axes of the tubes *B* and *D* are directed, at the same inclination, to the centre of one face of the prism, whilst the axis of the tube *C* is directed to the centre of the other face.

This arrangement makes the spectra produced by the light passing through *C*, and the image of the scale in *D* produced by total reflection, appear in one and the same spot, so that the positions occupied by the spectrum lines may be read off on the scale. The prism is placed in about that position in which there is a minimum divergence of the rays of the sodium line; and the telescope is set in that direction in which the red and the violet potassium lines are about equidistant from the middle of the field of view.

The colorless flame into which the flame-coloring bodies are to be introduced is placed 10 cm. from the slit. BUNSEN'S lamp, shown in Fig. 22, gives the best flame. The lamp is adjusted so as to place the upper border of the chimney about 20 mm. below the lower end of the slit. When this lamp has been lighted, and a bead of substance—say of potassium sulphate—introduced into the fusing zone by means of the holder shown in Fig. 27, the iron disk of the spectrum apparatus, which, with all it carries, is movable round its vertical axis, is turned until the point is reached where the luminosity of the spectrum is the most intense.

To cut off foreign light in all spectrum observations, the centre part of the apparatus is covered with a black cloth or box.

The spectra which are the most serviceable for analytical purposes are mapped on plate I. The scale employed is that of Kirchhoff and Bunsen's instrument, in which the degree 50 coincides with the yellow sodium line. The topmost scale gives the positions of some of the more important dark lines (Fraunhofer's) of the solar spectrum, which are distinguished by the letters *A*, *B*, and *a* and *b*, etc. The most characteristic or important lines are designated by the Greek numerals. Special notice of them is given in Section III.

In using the spectroscope it is not always sufficient to perceive a line with its appropriate color; its position with relation to known standards must be likewise ascertained. This is done by making for each spectroscope a diagram of the spectra, similar to plate I. For most purposes it is, however, only needful to map the more important lines. Any arbitrary scale being drawn, the lines are placed against degrees corresponding to those seen in the spectroscope when beads of the purest accessible compounds of the various alkali and

alkali-earth metals are placed in the flame. To insure uniformity the left edge of the sodium line, which is rarely absent even in specially prepared salts, is brought to coincide with the degree 50° or 100° of the scale of the instrument. To the position once adopted the scale must always be brought before taking observations, if by any means it has been disturbed.

With aid of the spectroscope we are able to detect quantities of substances that are not recognizable in any other manner. The results possess the utmost certainty, and are arrived at in a few moments.

APPENDIX TO SECTION I.

§ 18.

Apparatus.

The following list includes the articles actually required for the performance of simple experiments and investigations:

1. A Berzelius spirit lamp (§ 16, Fig. 14).
2. A glass spirit lamp (§ 16, Fig. 16). Or instead of these two, where coal-gas is procurable, a Bunsen's gas lamp—best one with chimney (§ 16, Figs. 17, 18, and 22).
3. A blowpipe (see § 15).
4. A platinum crucible which will contain about a quarter of an ounce of water, with a cover shaped like a shallow dish.
5. Platinum foil, as smooth and clean as possible, and not too thin; length about 40 mm.; width about 25 mm.
6. Platinum wire (see pp. 24 and 31). Three stronger wires and three finer wires are amply sufficient. They are kept most conveniently in a glass half filled with diluted acid; the wires may thus be kept clean.
7. A stand with twelve or more test-tubes. 16 to 18 cm. is the proper length of the tubes; from 1 to 2 cm. the proper width. The tubes must be made of thin white glass, and well annealed. The rim must be quite round, and slightly flared. The stand shown in Fig. 30 will be found most suitable.

8. SEVERAL NESTS OF BEAKERS AND A DOZEN SMALL FLASKS of thin, well annealed glass.

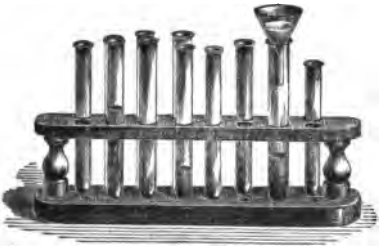


FIG. 30.

9. SEVERAL NESTS OF PORCELAIN EVAPORATING DISHES, AND A DOZEN SMALL PORCELAIN CRUCIBLES. Those of the royal manufacture of Berlin are unexceptionable, both in shape and durability.

10. SEVERAL GLASS FUNNELS of various sizes. They must be inclined at an angle of 60°, and merge into the neck at a definite angle.

11. A WASHING-BOTTLE of a capacity of from 500 to 800 c.c. (see § 7).

12. A FEW POUNDS OF GLASS TUBES AND SOME GLASS RODS. The former may be bent, drawn out, etc., over a Berzelius lamp or gas lamp; the latter are rounded at the ends by fusion.

13. A selection of WATCH GLASSES.

14. A small AGATE MORTAR.

15. A STEEL OR BRASS PINCERS about four or five inches long.

16. A WOODEN FILTER-STAND (see § 5).

17. A TRIPOD of thin iron, to support the dishes, etc., which it is intended to heat over the small spirit or gas lamp.

18. THE COLORED GLASSES described in § 17, especially blue and green.

SECTION II.

REAGENTS.

§ 19.

A VARIETY of phenomena may manifest themselves upon the decomposition or combination of bodies. In some cases liquids change their color; in others precipitates are formed; sometimes effervescence takes place, and sometimes deflagration, etc. Now, if these phenomena are very striking, and attend only upon the action of two definite bodies upon one another, it is obvious that the presence of one of these bodies may be detected by means of the other. If we know, for instance, that a white precipitate of certain definite properties is formed upon mixing baryta with sulphuric acid, it is clear that, if upon adding baryta to any liquid we obtain a precipitate exhibiting these properties, we may conclude that this liquid contains sulphuric acid.

Those substances which indicate the presence of others by any striking phenomena are called *reagents*.

According to the different objects attained by the application of these bodies, we make a distinction between *general* and *special reagents*. By *general reagents* we understand those which serve to determine the class or group to which a substance belongs; and by *special reagents* those which serve to detect bodies individually. That the line between the two divisions cannot be drawn with any degree of precision, and that one and the same substance is often made to serve both as a general and a special reagent, cannot well be held a valid objection to this classification, which is simply intended to induce a habit of employing reagents always for a settled purpose—viz., either simply to find out the *group* to which the substance belongs, or to determine the latter *individually*.

Whilst the usefulness of *general reagents* depends principally upon their efficiency in strictly characterizing groups of bodies, and often effecting a complete separation of the bodies belonging to one group from those belonging to another, that of *special reagents* depends upon their being

characteristic and sensitive. We call a reagent *characteristic* if the alteration produced by it, in the event of the body tested for being present, is so distinctly marked as to admit of no mistake. Thus iron is a characteristic reagent for copper, stannous chloride for mercury, because the phenomena produced by these reagents—viz., the separation of metallic copper and of globules of mercury—admit of no mistake. We call a reagent *sensitive* or *delicate* if its action is distinctly perceptible, even though a very minute quantity only of the substance tested for be present; such is, for instance the action of starch upon iodine.

Very many reagents are both characteristic and delicate; thus, for instance, hydrochlorauric acid for stannous salts, potassium ferrocyanide for ferric and cupric salts, etc.

I need hardly mention that, as a general rule, reagents must be chemically pure—*i.e.*, they must consist purely and simply of their essential constituents, and must contain no admixture of foreign substances. We must therefore make it an invariable rule to *test the purity of our reagents before we use them*, no matter whether they be articles of our own production or purchased. Although the *necessity* of this is fully admitted on all hands, yet we find that in *practice* it is too often neglected; thus it is by no means uncommon to see aluminium entered among the substances detected in an analysis, simply because the solution of sodium hydroxide used as one of the reagents happened to contain that element; or iron, because the ammonium chloride used was not free from that metal. The directions given in this section for testing the purity of the several reagents refer, of course, only to the presence of foreign matter resulting from the mode of their preparation, and not to mere accidental admixtures.

One of the most common sources of error in qualitative analysis proceeds from missing the proper measure—the right quantity—in the application of reagents. Such terms as "*addition in excess*," "*supersaturation*," etc., often induce novices to suppose that they cannot add *too much* of the reagent, and thus some will *fill* a test tube with acid, simply to supersaturate a few drops of an alkaline fluid, whereas *every drop* of acid added, after the neutralization point has once been reached, is to be looked upon as an excess of acid. On the other hand, the addition of an insufficient

amount is to be equally avoided, since a reagent added in insufficient quantity often produces phenomena quite different from those which will appear if the same reagent be added in excess: *e.g.*, a solution of mercuric chloride yields a *white* precipitate if tested with a *small* quantity of hydrogen sulphide; but if treated with the same reagent *in excess*, the precipitate is *black*. Experience has, however, proved that the most common mistake beginners make is to add the reagents too copiously. One reason why this over-addition must impair the accuracy of the results is obvious; we need simply bear in mind that the changes effected by reagents are perceptible within certain limits only, and that therefore they may be the more readily overlooked the nearer we approach these limits by diluting the fluid. Another reason is in the fact that a *large excess* of a reagent will often have a solvent or modifying action upon a precipitate or color, and will entirely prevent the exhibition of phenomena which a suitable quantity would without difficulty produce.

No special and definite rules can be given for avoiding this source of error; a general rule may, however, be laid down which will be found to answer the purpose, if not in all, at least in the great majority of cases. It is simply this: *Let the student always reflect before the addition of a reagent for what purpose he applies it, what are the phenomena he intends to produce, and what are the results of the addition of excess.*

We divide reagents into two classes, according to whether the fluidity which is indispensable for the action of reagents upon the various bodies, is brought about by the application of heat, or by means of liquid solvents; we have consequently, 1, *Reagents in. the wet way;* and 2, *Reagents in the dry way.* For greater clearness we subdivide these two principal classes as follows:

A. REAGENTS IN THE WET WAY.

I. Simple Solvents.

II. Coloring Matters and indifferent Vegetable Substances.

III. Acids and Halogens.

a. Oxygen acids.

b. Hydrogen acids and halogens.

c. Sulphur acids.

IV. BASES, METALS, and SULPHIDES.

a. Oxygen bases and metals.

b. Sulphides.

V. SALTS.

a. Of the alkali-metals.

b. Of the alkali-earth metals.

c. Of the heavy metals.

B. REAGENTS IN THE DRY WAY.

I. FLUXES.

II. BLOWPIPE REAGENTS.

A. REAGENTS IN THE WET WAY.

I. SIMPLE SOLVENTS.

Simple solvents are fluids which do not enter into chemical combination with the bodies dissolved in them; they will accordingly dissolve any quantity of matter up to a certain limit, which is called the point of saturation, and is in a measure dependent upon the temperature of the solvent. The essential and characteristic properties of the dissolved substances (taste, reaction, color, etc.) are not destroyed by the solvent. (See § 2.)

§ 20.

1. WATER, H_2O.

Preparation.—Pure water is obtained by distilling spring water from a copper still with head and condenser made of pure tin. The distillation is carried to about three-fourths of the quantity operated upon. If it is desired to have the distilled water perfectly free from carbonic acid and ammonium carbonate, the portions passing over first must be rejected. In the larger chemical laboratories, distilled water is obtained from the steam apparatus which serves for drying, etc. Rain water collected in the open air may in many cases be substituted for distilled water.*

* As regards the preparation of water absolutely free from organic matter, see STAS, Zeitschrift f. anal. Chem. 6, 417.

Tests.—It must be colorless, odorless, and tasteless, and should not leave the smallest residue when evaporated in a platinum vessel.* It should not be changed by ammonium sulphide (copper, lead, iron), nor rendered turbid by baryta water (carbonic acid). No cloudiness should be caused even after long standing by the addition of ammonium oxalate, of barium chloride and hydrochloric acid (sulphuric acid), of silver nitrate and nitric acid (chlorides), or of mercuric chloride and sodium carbonate (ammonia).

Uses.—We use water † principally as a simple solvent for a great variety of substances; the most convenient way of using it is with the washing-bottle (see § 7, Fig. 3), by which means a stronger or finer stream may be obtained. It serves also to effect the conversion of several neutral metallic salts (more particularly antimony trichloride and the salts of bismuth) into soluble acid and insoluble basic compounds.

§ 21.

2. Ethyl Alcohol, $C_2H_5 . OH$.

Preparation.—Two sorts of alcohol are used in chemical analyses: viz., 1st. Commercial "95 per cent. alcohol," which really contains 93 to 94 per cent. of alcohol by weight; and 2d, absolute alcohol. The latter may be prepared most conveniently by placing in a flask or tin can 800 grms. of good quick-lime in coarse powder or small lumps, adding 1 liter of "95 per cent. alcohol," connecting the vessel with the lower end of a condenser like Fig. 7, and keeping its contents boiling on a water bath for an hour. The can is then connected to the upper end of the condenser, and the dehydrated alcohol distilled off into a bottle for use.—Erlenmeyer; J. Lawrence Smith.

Tests.—Pure alcohol must completely volatilize, and ought not to leave a smell of fusel-oil when rubbed between the hands; nor should it alter the color of moist blue or red litmus paper. When kindled, it must burn with a faint bluish, barely perceptible flame.

* Ordinary distilled water rarely fails to leave some *slight* residue on evaporation; but this does not interfere with its ordinary uses in chemical analysis.—Ed.

† In analytical experiments we use only distilled water; whenever, therefore, the term *water* occurs in the present work, distilled water is meant.

Uses.—Alcohol serves (*a*) to effect the separation of bodies soluble in this fluid from others which do not dissolve in it, *e.g.*, of strontium chloride from barium chloride; (*b*) to precipitate from aqueous solutions many substances which are insoluble in dilute alcohol, *e.g.*, gypsum, calcium malate; (*c*) to produce various kinds of ether, *e.g.*, ethyl acetate, which is characterized by its peculiar and agreeable smell; (*d*) to reduce, mostly with the co-operation of an acid, certain peroxides and metallic acids, *e.g.*, lead dioxide, chromic acid, etc.; (*e*) to detect certain substances which impart a characteristic tint to its flame, especially boric acid, strontium, potassium, sodium, and lithium.

§ 22.

3. Ethyl Ether, $(C_2H_5)_2O$.

4. Chloroform, $CHCl_3$.

5. Carbon Disulphide, CS_2.

These solvents find but limited application in the qualitative analysis of inorganic bodies. They serve indeed almost exclusively to detect and isolate bromine and iodine. Chloroform and carbon disulphide are preferable to ether in this respect. The latter is used for the detection of chromic acid by means of hydrogen dioxide. These preparations are best procured by purchase.

Tests.—*Ether* must have a specific gravity of .713 at 20°, and require 9 parts of water for solution. The solution must not alter the color of test papers. Ether must, even at the common temperature, rapidly and completely evaporate on a watch-glass. *Chloroform* must be colorless and transparent and have a specific gravity of 1.48. It must have no acid reaction, nor impair the transparency of solution of nitrate of silver. Mixed with 2 vols. of water, and shaken, its volume must not appear perceptibly diminished. It must even at the common temperature readily and completely evaporate on a watch-glass. *Carbon disulphide* should be colorless, completely volatile even at the common temperature, and exercise no action upon lead carbonate. If

yellow, it may be purified by agitating with, and distilling from mercury.

II. COLORING MATTERS AND INDIFFERENT VEGETABLE SUBSTANCES.

§ 23.

1. Test Papers.

α. Blue Litmus Paper.

Preparation.—Digest 1 part of litmus of commerce with 6 parts of water, and filter the solution; divide the intensely blue filtrate into 2 equal parts; saturate the free alkali in the one part, by repeatedly stirring with a glass rod dipped in very dilute sulphuric acid, until the color of the fluid just appears red; add now the other part of the blue filtrate, pour the whole fluid into a dish, and draw strips of filter paper through it; suspend these slips over threads and leave them to dry. The color of litmus paper must be uniform, and neither too light nor too dark.

Uses.—Litmus paper serves to detect the presence of free acids, which change its blue color to red. It must be borne in mind, however, that many metallic salts produce the same effect.

β. Reddened Litmus Paper.

Preparation.—Stir blue solution of litmus with a glass rod dipped in dilute sulphuric acid, and repeat this process until the fluid has just turned distinctly red. Steep slips of paper in the solution, and dry them as in α. The dried slips must look distinctly red.

Uses.—Pure alkalies and alkaline earths, and also the sulphides of their metals, give a blue color to red litmus paper; alkali-carbonates and the soluble salts of several other weak acids, especially of boric acid, possess the same property. This reagent serves therefore for the detection of these bodies in general.

γ. Turmeric Paper.

Preparation.—Digest and heat 1 part of bruised turmeric

root with four parts of alcohol, and two of water; filter the tincture obtained, and steep slips of fine paper in the filtrate. The dried slips must exhibit a fine yellow tint.

Uses.—Turmeric paper serves for the detection of free alkalies, which change its yellow color to brown. It is not so delicate a test as the other reagent papers; but the change of color is highly characteristic, and is very distinctly perceptible in many *colored* fluids; we cannot well dispense, therefore, with this paper. When testing with turmeric paper, it is to be borne in mind that, besides the substances enumerated in β, several other bodies (boric acid, for instance) possess the property of turning its yellow color to brown-red. It affords an excellent means for the detection of the latter substance.

All test papers are cut into slips, which must be kept in well-closed boxes, or in black bottles away from light and fumes.

§ 24.

2. Solution of Indigo.

Preparation.—Take from 4 to 6 parts of fuming sulphuric acid, add slowly, and in small portions at a time, 1 part of finely pulverized indigo, taking care to keep the mixture well stirred. The acid has at first imparted to it a brownish tint by the matter which the indigo contains in admixture, but it subsequently turns deep blue. Elevation of temperature to any considerable extent must be avoided, as part of the indigo is thereby destroyed; it is therefore advisable, when dissolving larger quantities of the substance, to place the vessel in cold water. When the whole of the indigo has been added to the acid, cover the vessel, let it stand forty-eight hours, then pour its contents into 20 times the quantity of water, mix, filter and keep the filtrate for use.

Uses.—Indigo is decomposed by boiling with nitric acid, yellow-colored oxidation products being formed. It serves, therefore, for the detection of nitric acid. Solution of indigo is also well adapted to effect the detection of chloric acid and of free chlorine.

III. Acids and Halogens.

§ 25.

The acids which are used as reagents are soluble in water. The solutions taste acid and redden blue litmus paper, and are commonly designated by the simple name of the free acid, as the accession of water does not destroy their acid properties. Acids are divided into oxygen acids, sulphur acids and hydrogen acids.

[*Oxygen acids* (or *oxacids*) consist of acid or negative radicals united to hydrogen by means of oxygen. In other words, they are compounds of negative radicals with hydroxyl (OH). They are acid hydroxides.

Oxygen bases are composed of basic (positive) radicals with hydroxyl.

In most cases the *oxygen acids* may be formed by the reaction of an oxide of an electro-negative element (anhydride) upon water.

$$\underset{\text{Nitric pentoxide.}}{N_2O_5} + \underset{\text{Water.}}{H_2O} = \underset{\text{Nitric acid.}}{2(NO_2OH)}.$$

$$\underset{\text{Sulphur trioxide.}}{SO_3} + \underset{\text{Water.}}{H_2O} = \underset{\text{Sulphuric acid.}}{SO_2\langle^{OH}_{OH}}$$

The *oxygen bases*, or basic hydroxides, may also result from the action of an oxide of an electro-positive element upon water.

$$\underset{\text{Potassium monoxide.}}{K_2O} + H_2O = \underset{\text{Potassium hydroxide.}}{2\,KOH}.$$

Oxygen acids are *mono*, *di*, and *tri*, or more *basic*, and oxygen bases are *mon*, *di*, *tri*, and more *acid* according as they contain one, two, three, or more hydroxyls united respectively to univalent, bivalent, or trivalent radicals.

When oxygen acids act upon metallic oxides or hydroxides, the metal of the latter takes the place of hydrogen, and an *oxygen salt* is formed, while at the same time water is produced.

$$\underset{\text{Nitric acid.}}{NO_2OH} + \underset{\text{Potassium hydroxide.}}{KOH} = \underset{\text{Potassium nitrate.}}{NO_2OK} + \underset{\text{Water.}}{H_2O}.$$

$$\underset{\text{Sulphuric acid}}{SO_2(OH)_2} + \underset{\text{Potassium monoxide.}}{K_2O} = \underset{\text{Potassium sulphate.}}{SO_2(OK)_2} + H_2O, \text{ and}$$

$$SO_2(OH)_2 + \underset{\text{Potassium hydroxide.}}{KOH} = \underset{\text{Hydrogen potassium sulphate.}}{SO_2\langle{}^{OH}_{OK}} + H_2O$$

$$SO_2\langle{}^{OH}_{OH} + Zn\langle{}^{OH}_{OH} = \underset{\text{Zinc sulphate (normal.)}}{SO_2\langle{}^{O}_{O}\rangle Zn} + 2\,H_2O$$
Zinc hydroxide.

$$SO_2\langle{}^{OH}_{OH} + 2\left(Zn\langle{}^{OH}_{OH}\right) = \underset{\text{Zinc sulphate (basic.)}}{Zn\langle{}^{OH}_{O}{}^{O}_{O}\rangle Zn\langle{}^{OH}_{OH}} SO_2 + 2\,H_2O$$

By the mutual action of acids or negative oxides, and bases or positive oxides, three classes of salts are produced, viz., *normal, acid* and *basic. Normal salts* are those in which the acid and base saturate each other, in which, therefore, all the hydroxyls, whether of acid or base, are eliminated (in the form of water) and the acid radical remains united to metal by means of oxygen, *e.g.*, potassium nitrate and potassium and zinc sulphates (see above).

Acid salts are those which retain a part of the acid hydroxyl, *e.g.* hydrogen potassium sulphate. *Basic salts* are those in which a part of the hydroxyl of the base, or of the oxygen of the positive oxide, remains in the combination, *e.g.* basic zinc sulphate. (See above.)

The *reaction towards test papers* of soluble salts is either acid, neutral, or alkaline, according as the salt is acid, normal or basic, or according to the more or less pronounced acidity or basicity of the acid and basic radicals.—Ed.]

The *hydrogen acids* are formed by the combination of the halogens with hydrogen. Most of these possess the characteristic properties of acids in a high degree. They neutralize oxygen bases with formation of haloid salts and water; $2\,H\,Cl$ and $Na_2\,O = 2\,Na\,Cl$ and $H_2\,O$;— $6\,H\,Cl$ and $Fe_2\,O_3 = Fe_2\,Cl_6$ and $3\,H_2\,O$. The haloid salts produced by the action of powerful hydrogen acids upon strong bases have a neutral reaction; whilst the solutions of those haloid salts that con-

tain weakly basic elements (such as aluminium and iron) have an acid reaction.

[The *sulphur acids* may be regarded as compounds of negative radicals with hydrosulphuryl (S H); *e.g.* sulphocarbonic acid C S $(S H)_2$ and hydrosulphuric acid (hydrogen sulphide) H (S H). *Sulphur bases* are K (S H), Ca $(S H)_2$, etc. *Sulphur salts* result from the reaction of sulphur acids upon sulphur bases. Most sulphur salts, however, are produced by the action of negative anhydrosulphides on sulphur bases, or on positive anhydrosulphides, *e.g.*:

$$As_2 S_3 + 6 (K S H) = 2 [As S (S K)_3] + 3 H_2 S.$$

Arsenic sulphide. Potassium hydrosulphide. Potassium sulpharsenate. Hydrogen sulphide.—ED.]

§ 26.

1. SULPHURIC ACID, $H_2 S O_4$ or $S O_2 (O H)_2$.

We use—

a. Concentrated sulphuric acid of commerce.

b. Concentrated pure sulphuric acid.

The following methods may be recommended for preparing chemically pure sulphuric acid:

α. Put 1,000 grm. of ordinary concentrated sulphuric acid in a porcelain dish, add 3 grm. of sulphate of ammonium, and heat till copious fumes of sulphuric acid begin to escape, in order to destroy the oxides of nitrogen which are present. After cooling, add 4 or 5 grm. of powdered manganese dioxide, and heat to boiling with stirring, in order to convert any arsenious acid into arsenic acid. When cool pour off the clear fluid by means of a long funnel tube into a retort coated with clay. The retort should not be more than half full, and is to be heated directly over charcoal. To prevent bumping rest the retort on an inverted crucible cover, so that the sides may be more heated than the bottom. The neck of the retort must reach so far into the receiver that the acid distilling over drops directly into the body. To cool the receiver by means of water is unnecessary and even dangerous. To prevent the receiver coming into actual contact with the hot neck of the retort, some asbestos in large fibres is placed between them. When about 10 or 15 grm. has been drawn over, change the receiver and slowly distil off three-fourths

of the contents of the retort. This method depends on the fact discovered by BUSSY and BUIGNET, that on distilling sulphuric acid which contains arsenic in the form of arsenic acid an arsenic-free distillate is obtained.

β. Pour into 4 parts of water 1 part of concentrated sulphuric acid, and conduct into the mixture for some time a slow stream of hydrogen sulphide, keeping the fluid heated to 70°. Let the mixture stand at rest for several days, then decant the clear supernatant fluid from the precipitate, which consists of sulphur, lead sulphide, perhaps also arsenic sulphide, and heat the decanted fluid in a tubulated retort with upturned neck and open tubulature until sulphuric acid fumes escape with the aqueous vapor. The acid so purified is fit for many purposes of chemical analysis; if it is wished, however, to free it also from non-volatile substances, it may be distilled from a coated retort as in *α*. As soon as the drops in the neck of the retort become oily, the receiver is changed, and the concentrated acid which then passes over is kept in a separate vessel.

c. Common dilute sulphuric acid.—Add to 5 parts of water in a thin glass or porcelain dish gradually, and whilst stirring, 1 part of the concentrated sulphuric acid. The lead sulphate which separates is allowed to subside, and the clear fluid finally decanted.

Tests.—Pure sulphuric acid must be colorless; when colorless solution of ferrous sulphate is poured upon it in a test tube, no brown tint must mark the plane of contact of the two fluids (nitric acid, nitrous acid); when diluted with twenty parts of water it must not impart a blue tint to a solution of potassium iodide (see § 158) mixed with starch paste (nitrous acid). Mixed with pure zinc and water, it must yield hydrogen gas, which, on being passed through a red hot tube, must not deposit the slightest trace of arsenic. It must leave no residue upon evaporation on platinum, and must remain perfectly clear upon dilution with four or five parts of alcohol (lead, iron, calcium). The presence of small quantities of lead is detected most easily by adding some hydrochloric acid to the sulphuric acid in a test tube. If the plane of contact is marked by turbidity (lead chloride), lead is present. Sulphurous acid is discovered by the odor after shaking the acid in a half filled bottle.

Uses.—Sulphuric acid has for most bases a greater affinity than almost any other acid; it is therefore used principally for the liberation and expulsion of other acids, especially phosphoric, boric, hydrochloric, nitric, and acetic acids. Oxalic acid and many other substances are decomposed when brought into contact with concentrated sulphuric acid. The nature of the decomposed body may in such cases be inferred from the products of decomposition. Sulphuric acid is also used for the evolution of certain gases, more particularly of hydrogen and hydrogen sulphide. It serves also as a special reagent for the detection and precipitation of barium, strontium, and lead.

§ 27.

2. Nitric Acid, HNO_3 or $NO_2.OH$.

Preparation.—*a.* Heat crude nitric acid of commerce, as free as possible from chlorine, and of a specific gravity of at least 1.31,* in a glass retort to boiling, with addition of some potassium nitrate; let the distillate run into a receiver kept cool, and try from time to time whether after dilution it still continues to precipitate or cloud solution of silver nitrate. As soon as this ceases to be the case, change the receiver, and distil until a trifling quantity only remains in the retort. Dilute the distillate with water until the specific gravity is 1.2.

b. Dilute crude nitric acid of commerce of about 1.38 specific gravity with two-fifths of its weight of water, and add solution of silver nitrate as long as a precipitate of silver chloride continues to form; then add a further slight excess of solution of silver nitrate, let the precipitate subside, decant the perfectly clear supernatant acid into a retort or an alembic with ground head; add some potassium nitrate free from chlorine, and distil until only a small quantity remains, taking care to attend to the proper cooling of the fumes distilling over. Dilute the distillate, if necessary, with water until it has a specific gravity of 1.2.

* A weaker acid will not answer the purpose. The "parting acid" used in Assay Offices, of sp. gr. 1.4, commonly contains no impurities but a trace of chlorine, and answers for most analytical uses.

Tests.—Pure nitric acid must be colorless and leave no residue upon evaporation on platinum foil. Solution of silver nitrate or of barium nitrate must not cause the slightest turbidity in it. Dilute the acid with water before adding these reagents, as otherwise nitrates will precipitate. Silver should be tested for by hydrochloric acid.

Uses.—Nitric acid serves as a chemical solvent for metals, oxides, sulphides, oxygen salts, etc. With metals and sulphides of metals the acid first oxidizes the metal present, at the expense of part of its own oxygen, and dissolves it as nitrate. Most oxides are dissolved by nitric acid at once as nitrates; and so are also most of the insoluble salts with weaker acids, the latter being expelled in the process by the nitric acid. Nitric acid dissolves also salts with soluble non-volatile acids, as, *e.g.*, calcium phosphate, with which it forms calcium nitrate and acid calcium phosphate. Nitric acid is used also as an oxidizing agent: for instance, to convert ferrous oxide into ferric oxide, stannous oxide into stannic oxide, etc.

§ 28.

3. Acetic Acid, $C_2H_4O_2$ or $CH_3.COOH$.

The No. 8 acetic acid of commerce, which contains 30 per cent. of $C_2H_4O_2$, and has a specific gravity of 1.04, answers most purposes of analysis.

Tests.—Pure acetic acid must leave no residue upon evaporation, and—after saturation with sodium carbonate—emit no empyreumatic odor. Hydrosulphuric acid, solution of silver nitrate, and solution of barium nitrate must not color or cloud the dilute acid, nor must ammonium sulphide after neutralization of the acid by ammonia. Solution of indigo must not lose its color when heated with the acid. Empyreumatic matter is best detected by neutralizing the acid with sodium carbonate, and adding solution of potassium permanganate. If the solution loses its color and afterwards deposits a brown precipitate, empyreumatic matter is present.

If the acid is not pure, add some sodium acetate and redistil from a glass retort not quite to dryness; if it contains sulphur dioxide (in which case hydrogen sulphide will pro-

duce a white turbidity in it), digest it first with lead dioxide or finely pulverized manganese dioxide, and then distil with sodium acetate.

Uses.—Acetic acid possesses a greater solvent power for some substances than for others; it is used therefore to distinguish the former from the latter; thus it serves to distinguish calcium oxalate from calcium phosphate. Acetic acid is used also to acidulate fluids where it is wished to avoid the employment of mineral acids.

§ 29.

4. Tartaric Acid, $C_4H_6O_6$.*

The tartaric acid of commerce is sufficiently pure. It is kept in powder, as its solution suffers decomposition after a time. For use it is dissolved in a little water with the aid of heat.

Uses.—The addition of tartaric acid to solutions of salts of various metals, especially of iron and aluminium, prevents the usual precipitation of these metals by an alkali; this non-precipitation is owing to the formation of double tartrates, which are not decomposed by alkalies.

Tartaric acid may therefore be employed to effect the separation of these metals from others the precipitation of which it does not prevent. Tartaric acid forms a difficultly soluble salt with potassium, but not so with sodium; it is therefore one of our best reagents to distinguish between the two metals. *Acid sodium tartrate* answers this latter purpose still better than the free acid. This reagent is prepared by dissolving one of two equal portions of tartaric acid in water, neutralizing with sodium carbonate, then adding the other portion of the acid, and evaporating the solution to the crystallization point. For use, 1 part of the salt is dissolved in 10 parts of water.

* Or $\begin{matrix} CH(OH)—COOH \\ | \\ CH(OH)—COOH. \end{matrix}$

b. Hydrogen Acids and Halogens.

§ 30.

1. Hydrochloric Acid or *Hydrogen Chloride*, H Cl.

Preparation.—Pour a cooled mixture of seven parts of concentrated sulphuric acid and two parts of water over four parts of sodium chloride in a retort; expose the retort, with slightly raised neck, to the heat of a sand-bath until the evolution of gas ceases; conduct the evolved gas, by means of a bent tube, into a flask containing six parts of water, and take care to keep this vessel constantly cool. To prevent the gas from receding the tube ought to dip but about one line into the water of the flask. When the operation is terminated, try the specific gravity of the acid produced, and dilute with water until it marks from 1.11 to 1.12. If you wish to insure the absolute purity of the acid, and its perfect freedom from every trace of arsenic and chlorine, you must take care to free the sulphuric acid intended to be used in the process from arsenic and the oxygen compounds of nitrogen, according to the directions of § 26. A pure acid may also be prepared cheaply from the crude hydrochloric acid of commerce by diluting the latter to a specific gravity of 1.12, and distilling the fluid, with addition of some chloride of sodium. Or you may put the acid into the retort in the concentrated form, placing 60 parts of water into the receiver for every 100 parts of concentrated acid, and not luting the receiver to the retort. If the crude acid contains chlorine, this should be removed first by cautious addition of solution of sulphur dioxide, before proceeding to the distillation; if, on the other hand, it contains sulphur dioxide, this is removed in the same way by cautious addition of some chlorine water. Hydrochloric acid not unfrequently contains arsenious chloride, owing to the presence of arsenic in the sulphuric acid employed. To free it from this impurity, the acid is mixed with twice its volume of water, hydrogen sulphide is conducted into it, the mixture allowed to stand at rest for some time, the clear fluid then decanted from the sulphur and arsenious sulphide, and heated, to expel the hydrogen sulphide.

Tests.—Hydrochloric acid must be perfectly colorless and leave no residue upon evaporation. If it turns yellow on evaporation, ferric chloride is present. It must not impart a blue tint to a solution of potassium iodide mixed with starch paste (chlorine or ferric chloride), nor discolor a fluid made faintly blue with iodized starch (sulphur dioxide). Barium chloride ought not to produce a precipitate in the highly diluted acid (sulphuric acid). Hydrogen sulphide must leave the diluted acid unaltered (arsenic). After neutralization with ammonia, ammonium sulphide must produce no change in it (iron, thallium).

Uses.—Hydrochloric acid serves as a solvent for many substances. It dissolves many metals and sulphides of metals as chlorides, with evolution of hydrogen or of hydrogen sulphide. It dissolves metallic oxides and peroxides in the form of chlorides, in the latter case mostly with liberation of chlorine. Salts with insoluble or volatile acids are also converted by hydrochloric acid into chlorides, with separation of the original acid; thus calcium carbonate is converted into calcium chloride, with liberation of carbon dioxide. Hydrochloric acid dissolves salts with non-volatile and soluble acids apparently without decomposing them (*e.g.* calcium phosphate); but the fact is that in cases of this kind a metallic chloride and a soluble acid salt of the acid of the dissolved compound are formed; thus, for instance, in the case of calcium phosphate, calcium chloride and acid calcium phosphate are formed. With salts of acids forming no soluble acid compound with the base present, hydrochloric acid forms metallic chlorides, the liberated acids remaining free in solution (calcium borate). Hydrochloric acid is also applied as a special reagent for the detection and separation of silver, mercury and lead, and likewise for the detection of free ammonia, with which it produces in the air dense white fumes of ammonium chloride.

§ 31.

2. Chlorine, (Cl) and Chlorine Water.

Preparation.—Mix 18 parts of common salt in lumps with 15 parts of *finely pulverized* good manganese dioxide, free

from calcium carbonate; put the mixture in a flask, pour a *completely cooled* mixture of 45 parts of concentrated sulphuric acid and 21 parts of water upon it, and shake the flask: a uniform and continuous evolution of chlorine gas will soon begin, which, when slackening, may be easily increased again by the application of a *gentle* heat. This method of WIGGERS is excellent, and can be highly recommended. Conduct the chlorine gas evolved first through a flask containing a little water, then into a bottle filled with cold water, and continue the process until the fluid is saturated. Where it is desired to obtain chlorine water quite free from bromine, the washing flask is changed after about one-half of the chlorine has been expelled, and the gas which now passes over is conducted into a fresh bottle filled with water. If the chlorine water is to be quite free from hydrochloric acid, the gas must be passed through a U tube containing manganese dioxide. The chlorine water must be protected from the action of light; since, if this precaution is neglected, it speedily suffers complete decomposition, being converted into dilute hydrochloric acid, with evolution of oxygen (resulting from the decomposition of water). Smaller quantities, intended for use in the laboratory, are best kept in a stoppered bottle, protected by a case of pasteboard. Chlorine water which has lost its strong peculiar odor is unfit for use.

Uses.—Chlorine has a greater affinity than iodine and bromine for metals and for hydrogen. Chlorine water is therefore an efficient agent to effect the expulsion of iodine and bromine from their compounds. Chlorine serves moreover to effect the solution of certain metals (gold, platinum), to decompose metallic sulphides, to convert sulphurous acid into sulphuric acid, ferrous into ferric oxide, etc., and also to effect the destruction of organic substances, as in presence of these it withdraws hydrogen from the water, enabling thus the liberated oxygen to combine with the vegetable matters and to effect their decomposition. For this latter purpose it is often advisable to evolve the chlorine in the fluid which contains the organic substances; this is effected by adding hydrochloric acid to the fluid, heating the mixture, and then adding potassium chlorate. This gives rise to the formation of potassium chloride, water, free chlorine, and chlorine tetroxide, which acts in a similar manner to chlorine.

§ 32.

3. Nitro-Hydrochloric Acid. *Aqua regia.*

Preparation.—Mix 1 part of pure nitric acid with from 3 to 4 parts of pure hydrochloric acid.

Uses.—Nitric acid and hydrochloric acid decompose each other, the decomposition mostly resulting, as Gay-Lussac has shown, in the formation of two compounds which are gaseous at the ordinary temperature, N O Cl_3 and N O Cl, and of free chlorine and water. Thus, 2 (N O_2. O H) + 6 (H Cl) = 4 (H_2 O) + N O Cl + N O Cl_2 + 3 Cl). This decomposition ceases as soon as the fluid is saturated with the gas; but it recommences the instant this state of saturation is disturbed by the application of heat or by decomposition of the acid. The presence of the free chlorine, and also, but in a subordinate degree, that of the acids named, makes aqua regia our most powerful solvent for metals (with the exception of those which form insoluble compounds with chlorine). Nitro-hydrochloric acid serves principally to effect the solution of gold and platinum, which metals are insoluble both in hydrochloric and in nitric acid; and also to decompose various metallic sulphides, *e.g.* cinnabar, pyrites, etc.

§ 33.

4. Hydrofluosilicic Acid, H_2 Si F_6.

Preparation.—Take 1¼ parts of powdered glass, or 1 part of powdered ignited flint, or 1 part of quartz sand. Whichever is used, it must have been washed from every particle of dust, and then ignited. Mix intimately with one part of perfectly dry fluor spar in powder; pour nine parts of concentrated sulphuric acid over the mixture in a non-tubulated retort, which it is advisable to coat with clay, and mix carefully by shaking the vessel. As the mixture swells up when getting warm, it must at first fill the retort only to one-third. The neck of the retort is connected air-tight with a small tubulated receiver, and the tubulus of the latter again, by means of India-rubber, with a wide glass tube twice bent at right angles. To the descending limb of the glass tube a

funnel is attached by means of India-rubber; this funnel is lowered into a beaker containing four parts of water. Promote the disengagement of gaseous silicon fluoride, which commences even in the cold, by moderately heating the retort over charcoal. Towards the end of the process a pretty strong heat should be applied. Every gas bubble produces in the water a precipitate of silicic acid, with simultaneous formation of hydrofluosilicic acid, $3\ Si\ F_4 + 2\ H_2\ O = 2\ H_2\ Si\ F_6 + Si\ O_2$. The precipitated silicic acid renders the liquid gelatinous, and it is for this reason that the aperture of the descending limb of the tube cannot be allowed to dip direct into the water, since it would in that case speedily be choked. It sometimes happens in the course, and especially towards the end of the operation, that complete channels of silicic acid are formed in the gelatinous liquid, through which the gas gains the surface without undergoing decomposition if the liquid is not occasionally stirred. When the evolution of gas has completely ceased, throw the gelatinous paste upon a linen cloth. Squeeze the fluid through, and filter it afterwards. Keep the filtrate for use.

Tests.—Hydrofluosilicic acid must produce no precipitate in solutions of salts of strontium (strontium sulphate).

Uses.—Bases decompose with hydrofluosilicic acid, forming water and metallic silicofluorides. Many of these are insoluble, whilst others are soluble; the latter may therefore by means of this reagent be distinguished from the former. In the course of analysis hydrofluosilicic acid is applied simply for the detection and separation of barium.

c. Sulphur Acids.

§ 34.

1. Hydrogen Sulphide. *Hydrosulphuric Acid. Sulphuretted Hydrogen*, H_2S.

Preparation.—Hydrogen sulphide is usually evolved from iron sulphide, which is broken into small lumps and then treated with dilute sulphuric or hydrochloric acid. Fused iron sulphide may be purchased cheaply, or may be made by heating iron turnings, or 1 to 1½ inch iron nails, in a covered

Hessian crucible to a white heat, and then adding small lumps of roll-sulphur until the entire contents of the crucible are in fusion. As soon as this is the case, pour the fused mass upon sand, or into an old Hessian crucible. Or make a hole in the bottom of the crucible, when the iron sulphide will run through as fast as it forms, and may be received in a shovel placed in the ash-pit. Or introduce an intimate mixture of thirty parts of iron filings and twenty-one parts of flowers of sulphur in small portions into a red-hot crucible, awaiting always the incandescence of the portion last introduced before proceeding to the addition of a fresh one. When you have thus put the whole mixture into the crucible, cover the latter closely, and expose it to a more intense heat, sufficient to make the iron sulphide fuse more or less.

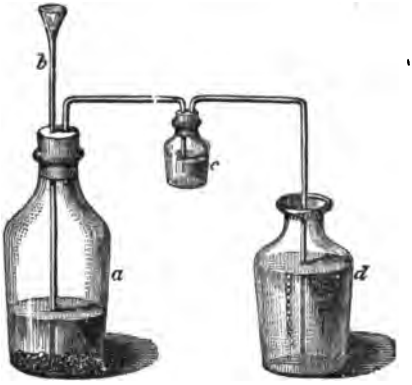


FIG. 32.

The evolution of the gas may be effected in the apparatus illustrated by Fig. 32. Pour water over the iron sulphide in *a*; add concentrated hydrochloric or sulphuric acid, and shake the mixture; the evolved gas is washed in *c*. When a sufficient quantity of gas is evolved, pour the fluid off the still undecomposed iron sulphide, rinse the bottle repeatedly with water, then fill it partly with that fluid, and keep it for the next operation.

FIG. 33.

For larger laboratories, or for chemists having to operate often and largely with hydrogen sulphide, Kipp's well known apparatus may be used, Fig. 33. The upper globe should be large, and its neck should not reach too near the base of the lower reser-

voir. This neck should carry a washer or collar of caoutchouc at the base of the middle globe to keep the iron sulphide *b* from falling into *d*.

In the MOHR apparatus, Fig. 34, the glass vessel A (commonly used for desiccating gases) has a perforated disk of lead or caoutchouc at *b*, and above is nearly filled with lumps of fused iron sulphide. To the end of *d* is fixed, by means of India-rubber, *a*, a small piece of wide glass tube, which is filled with cotton, and is intended to stop any particles of liquid which may be spirted up. *c* is a glass cock with a long wooden handle; *e* contains a solution of sodium carbonate,

FIG. 34.

to prevent the escape of sulphuretted hydrogen. The acid used in *B* is a mixture of common hydrochloric acid with two measures of water.

To obtain a stream of H_2S with this apparatus, *B* is put upon the shelf, as in the figure, and the cock at *c* is opened. When not in use *B* is set upon the table so that the partially saturated acid in the base of *A* may be renewed.

[A very cheap and effective self-regulating apparatus is

shown in Fig. 35. It is made from a two-quart fruit-bottle, in whose neck the chimney of a student lamp is suspended by means of a wide cork; a disk of perforated lead plate or a perforated cork rests on the constriction in the chimney; the latter is then nearly filled with lumps of fused ferrous sulphide; above this a wad of moist sponge to wash the gas is placed, and to the chimney is fitted a rubber stopper, bent tubes joined by rubber, and a screw-clamp, as in the figure, or preferably a tube with glass stopcock. A rubber band stretched over the lower rim of the chimney may avert fracture in disjointing the apparatus.

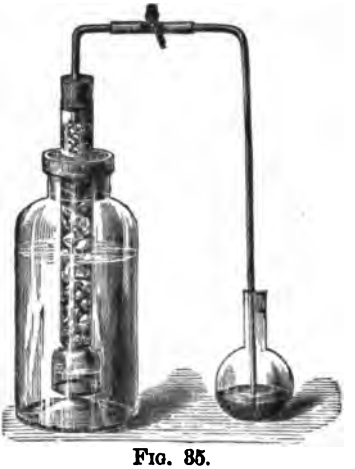


Fig. 35.

The bottle being nearly filled with a mixture of equal vols. commercial hydrochloric acid and water, is ready for use.—Ed.]

Sulphuretted hydrogen water (*hydrogen sulphide solution*) is usually prepared by conducting the gas into very cold water, which has been previously freed from air by boiling. The operation is continued until the water is saturated with the gas, which may be readily ascertained by closing the mouth of the flask with the thumb, and shaking it a little; if upon this a pressure is felt from within, the operation may be considered at an end. Sulphuretted hydrogen water must be kept in well-closed vessels, otherwise it will soon suffer decomposition, the hydrogen being oxidized to water, and a small portion of the sulphur to sulphuric acid, the rest of the sulphur separating.

Pure sulphuretted hydrogen water must be perfectly clear and strongly emit the odor of the gas; when treated with ferric chloride, it must yield a copious precipitate of sulphur. Addition of ammonia must not impart a blackish appearance to it. It must leave no residue upon evaporation on platinum.

Uses.—Hydrogen sulphide has a strong tendency to undergo decomposition with metallic oxides, forming water and metallic sulphides, which latter being mostly insoluble in water

are usually precipitated in the process. By modifying the conditions of precipitation we may divide the whole of the precipitable metals into groups, as will be found explained in Section III. Some of the precipitated sulphides exhibit characteristic colors indicative of the individual metals which they contain. The great facility with which hydrogen sulphide is decomposed renders this substance also a useful reducing agent for many compounds; thus it serves, for instance, to reduce ferric salts to ferrous salts, chromic acid to chromic oxide, etc. In these reductions the sulphur separates in the form of a fine white powder. Whether the hydrogen sulphide had better be applied in the gaseous form or in aqueous solution depends upon circumstances.

§ 35.

IV. Bases, Metals, and Sulphides.

Bases are divided into oxygen bases and sulphur bases (see § 25).

The *oxygen bases and the corresponding oxides* are classified into alkalies, alkali-earths, earths proper, and oxides or hydroxides of the heavy metals. The alkalies are readily soluble in water; the alkali-earths dissolve with greater difficulty in that menstruum; and magnesia, the last member of the class, is only very sparingly soluble in it. The earths proper and the oxides and hydroxides of the heavy metals are insoluble in water or nearly so (except thallious hydroxide). The solutions of the alkalies and alkali-earths are caustic when sufficiently concentrated; they have an alkaline taste, change the yellow color of turmeric paper to brown, and restore the blue tint of reddened litmus paper; they saturate acids completely, so that even the salts which they form with strong acids do not change vegetable colors, whilst those with weak acids generally have an alkaline reaction. The earths proper and the hydroxides and oxides of the heavy metals combine likewise with acids to form salts, but, as a rule, they do not entirely take away the acid reaction of the latter.

The *sulphur bases* containing the metals of the alkalies and alkali-earths are soluble in water. The solutions have a

strong alkaline reaction. The other sulphur bases do not dissolve in water.

a. Oxygen Bases.

α. Alkalies.

§ 36.

1. Potassium Hydroxide, or Potassa, K O H, and Sodium Hydroxide, or Soda, Na O H.*

The preparation of perfectly pure potassa or soda is a difficult operation. It is advisable, therefore, to provide, besides perfectly pure caustic alkali, also some which is not quite pure, and some which, being free from certain impurities, may in many cases be safely substituted for the pure substance.

a. Common solution of soda.—Put into a clean cast-iron pan provided with a lid, 3 parts of crystallized sodium carbonate of commerce and 15 parts of water, heat to boiling, and add, in small portions at a time, thick milk of lime prepared by pouring 3 parts of warm water over 1 part of fresh-burned quicklime and letting the mixture stand in a covered vessel until the lime is reduced to a uniform pulpy mass. Keep the liquid in the pan boiling whilst adding the milk of lime, and for a quarter of an hour longer; then filter off a small portion, and try whether the filtrate still causes effervescence in hydrochloric acid. If this is the case, the boiling must be continued, and if necessary some more milk of lime must be added to the fluid. When the solution is perfectly free from carbonic acid, cover the pan, allow the fluid to cool a little, and then draw off the nearly clear solution from the residuary sediment, by means of a siphon filled with water, and transfer it to a glass flask. Boil the residue a second and a third time with water, and draw off the fluid in the same way. Cover the flask close with a glass plate, and allow the lime suspended in the fluid to subside completely. Scour the iron pan clean, pour the clear solution back into it, and evaporate

* Also termed potassium hydrate and sodium hydrate.

it to 6 or 7 parts. The solution so prepared contains from 9 to 10 per cent. of soda, and has a specific gravity of from 1.13 to 1.15. If it is wished to filter a solution of soda which is not quite clear, a covered funnel should be used, which has been charged first with lumps of white marble and then with powder of the same, the fine dust being rinsed out with water before the filter is used (GRAEGER). Solution of soda must be clear, colorless, and as free as possible from carbonic acid; ammonium sulphide must not impart a black color to it. Traces of silicic acid, alumina, and phosphoric acid are usually found in a solution of soda prepared in this manner; on which account it is unfit for use in accurate experiments. Solution of soda is kept best in bottles closed with ground glass caps. In default of capped bottles, common ones with well-ground stoppers may be used, in which case the neck must be wiped perfectly dry and clean inside and the stopper coated with paraffine; since, if this precaution is neglected, it will be found impossible after a time to remove the stopper, particularly if the bottle is only rarely opened.

b. Potassa purified with alcohol.—Dissolve some caustic potassa of commerce in alcohol, in a stoppered bottle, by digestion and shaking; let the fluid stand, decant it, or filter it if necessary, and evaporate the clear fluid in a silver dish over the gas or spirit lamp until no more vapors escape; adding from time to time, during the evaporation, some water to prevent blackening of the mass. Place the silver dish in cold water until it has sufficiently cooled; remove the cake of potassa from the dish, break it into coarse lumps in a hot mortar, and keep in a well-closed glass bottle. When required for use, dissolve a small lump in water.

The potassa so prepared is sufficiently pure for most purposes; it contains, indeed, a minute trace of alumina, but is usually free from phosphoric, sulphuric, and silicic acids. The solution must remain clear upon addition of ammonium sulphide; hydrochloric acid must only produce a barely perceptible effervescence in it. The solution acidified with hydrochloric acid must, upon evaporation to dryness, leave a residue which dissolves in water to a clear fluid. The solution acidified with hydrochloric acid, and then mixed with ammonia in the least possible excess, must not show any flocks of alumina, at least until it has stood in a warm place

for several hours. The solution acidified with nitric acid must not give any precipitate with a nitric acid solution of ammonium molybdate.

c. Potassa prepared with baryta.—Dissolve pure crystals of baryta (§ 38) by heating with water, and add to the solution pure potassium sulphate until a portion of the filtered fluid, acidified with hydrochloric acid and diluted, no longer gives a precipitate on addition of a further quantity of the sulphate (16 parts of crystals of baryta require 9 parts of potassium sulphate). Let the turbid fluid clear, decant, and evaporate in a silver dish as in *b*. The potassa so prepared is perfectly pure, except that it contains a trifling admixture of potassium sulphate, which is left behind upon dissolving in a little water. It is but rarely required, its use being in fact exclusively confined to the detection of minute traces of aluminium.

[*d. Absolutely pure soda* is best prepared by dissolving sodium in pure water in a silver dish and evaporating until a drop of the liquid solidifies on cooling. This preparation is now to be had in commerce.—ED.]

Uses.—The great affinity which the fixed alkalies possess for acids renders these substances powerful agents to effect the decomposition of the salts of most bases, and consequently the precipitation of those bases or oxides which are insoluble in water. Many of the so precipitated hydroxides redissolve in an excess of the precipitant, as, for instance, those of aluminium, chromium, and lead; whilst others remain undissolved, as those of iron, bismuth, etc. The fixed alkalies serve therefore also as a means to separate the former from the latter. Potassa and soda dissolve also many salts (*e.g.*, lead chromate, sulphur compounds, etc.), and contribute thus to separate and distinguish them from other substances. Many of the hydroxides and oxides precipitated by the action of potassa or soda exhibit peculiar colors, or possess other characteristic properties that may serve to lead to the detection of the individual metal which they respectively contain; such are, for instance, the precipitates of manganous hydroxide, ferrous hydroxide, mercurous oxide, etc. The fixed alkalies expel ammonia from its salts, and enable us thus to detect that body by its smell, its action on vegetable colors, etc.

§ 37.

2. Ammonia, NH_3. Ammonium Hydroxide, NH_4OH.

Preparation.—Ammonia is obtainable in commerce in a very pure state.* For preparing it on a small scale the following method answers well. Introduce into a flask 4 parts of ammonium chloride, either crystallized or in coarse powder, and the dry slacked lime prepared from 5 parts of quicklime; mix by shaking, and cautiously add enough water to make the powder agglomerate into lumps. Set the flask in a sand bath and connect it with a rather large wash-bottle, and delivery tube. Put a small quantity of water in the wash-bottle and about 10 parts of water in the flask destined to absorb the gas. Place the latter in cold water, and then begin to apply heat. Evolution of gas speedily sets in. Continue to heat until no more bubbles appear. Open the cork of the flask to prevent the receding of the fluid. The solution of ammonia contained in the washing bottle is impure, but that contained in the receiver is pure; dilute it with water until the specific gravity is about .96 = 10 per cent. of ammonia. Keep the fluid in bottles closed with ground stoppers.

Tests.—Solution of ammonia must be colorless, and ought not to leave the least residue when evaporated in a platinum dish. When heated with an equal volume of lime water, it should cause no turbidity, at least not to a very marked extent (carbonic acid).

[*Concentrated* ammonia precipitates lime water, and must be diluted before applying this test for carbonic acid.—Ed.]

When supersaturated with nitric acid, neither solution of barium nitrate nor of silver nitrate must render it turbid, nor must hydrogen sulphide impart to it the slightest color.

Uses.—Solution of ammonia, although formed by conducting ammoniacal gas (NH_3) into water and suffering escape of that gas upon exposure to the air, and much quicker when heated, may be regarded as a solution of hydroxide of ammonium (NH_4OH) in water, the first acceding molecule of water H_2O being assumed to form NH_4OH with NH_3. Upon this assumption solution of ammonia may be looked upon as an analogous fluid to solution of potassa and solution of soda, which greatly simplifies the explanation of all its re-

* Of Bela Clapp, Pawtucket, R. I.

actions, the salts resulting from the neutralization of oxygen acids by solution of ammonia being assumed to contain ammonium NH_4 instead of NH_3. Ammonia is one of the most frequently used reagents. It is especially applied for the saturation of acid fluids, and also to effect the precipitation of a great many metallic hydroxides; many of these precipitates redissolve in an excess of ammonia, as, for instance, the hydroxides of zinc, cadmium, silver, copper, etc., whilst others are insoluble in free ammonia. This reagent may therefore serve also to separate and distinguish the former from the latter. Some of these precipitates, as well as their solutions in ammonia, exhibit peculiar colors, which may at once lead to the detection of the metal which they contain.

Many of the hydroxides which are precipitated by ammonia from neutral solutions are not precipitated by this reagent from acid solutions, their precipitation from the latter being prevented by the ammonium salt formed in the process. Compare § 56.

β. Alkali Earths.

§ 38.

1. Barium Hydroxide, or Baryta, $Ba(OH)_2$.

Preparation.—There are many ways of preparing baryta; but as witherite (barium carbonate) is now cheaply procurable, I prefer the following: Mix intimately together 100 parts of finely pulverized witherite, 10 parts of charcoal in powder, and 5 parts of rosin, put the mixture in an earthenware crucible, lute on the lid with clay, and expose the crucible so prepared to the heat of a brick-kiln. Break and triturate the baked mass, boil repeatedly with water in an iron pot, filter into bottles, stopper, and let them stand in the cold, when large quantities of crystals of barium hydroxide $Ba(OH)_2 + 8H_2O$ will make their appearance. Let the crystals drain in covered funnels, dry rapidly between sheets of blotting paper, and keep them in well-closed bottles. For use dissolve 1 part of the crystals in 20 parts of water, with the aid of heat, and filter the solution. The *baryta water* so prepared is purer than the mother liquor running off from the crystals. The residue, which is insoluble in water and

consists of undecomposed witherite and charcoal, may be turned to account in the preparation of barium chloride.

Tests.—Baryta water must, after precipitation of the barium by pure sulphuric acid, give a filtrate remaining clear when mixed with alcohol, and leaving no fixed residue upon evaporation in the platinum crucible.

Uses.—Barium hydroxide being a strong base, precipitates the metallic hydroxides insoluble in water from the solutions of their salts. In the course of analysis we use it simply to precipitate magnesia. Baryta water may also be used to precipitate those acids which form insoluble barium compounds; it is applied with this view to effect the detection of carbonic acid, the removal of sulphuric acid, phosphoric acid, etc.

§ 39.

2. Calcium Hydroxide, or Lime, $Ca(OH)_2$.

Calcium hydroxide is obtained by slacking lumps of pure calcined lime in a porcelain dish, with half their weight of water. The heat which accompanies the combination of the lime and the water is sufficient to evaporate the excess of water. Slacked lime must be kept in a well-stoppered bottle.

To prepare *lime water*, digest slacked lime for some time with cold distilled water, shaking the mixture occasionally; let the undissolved portion of lime subside, decant, and keep the clear fluid in a well-stoppered bottle. If it is wished to have the lime water quite free from all traces of alkalies, baryta and strontia, which are almost invariably present in slacked lime prepared from calcined limestone, the liquids of the first two or three decantations must be removed, and the fluid decanted afterwards alone made use of.

Tests.—Lime water must impart a strongly marked brown tint to turmeric paper, and give a not too inconsiderable precipitate with sodium carbonate. It speedily loses these properties upon exposure to the air, and is thereby rendered totally unfit for analytical purposes.

Uses.—Lime forms with many acids insoluble, with others soluble salts. Lime-water may therefore serve to distinguish the former acids, which it precipitates from their solutions,

from the latter, which it will of course fail to precipitate. Many of the precipitable acids are thrown down only under certain conditions, *e.g.*, on boiling (citric acid), which affords a ready means of distinguishing between them by altering these conditions. We use lime water in analysis principally to effect the detection of carbonic acid, and also to distinguish between citric acid and tartaric acid. Slacked lime is chiefly used to liberate ammonia from ammonium salts.

γ. Heavy Metals and their Oxides and Hydroxides.

§ 40.

1. Zinc, Zn.

Select zinc of good quality and, above all, perfectly free from arsenic. The method described § 132, 10, will serve to detect the presence of the slightest trace of this substance. Fuse the metal and pour it in a thin stream into a large vessel with water. Zinc which contains arsenic must be rejected, for no practicable process of purification is known (Eliot and Storer).*

Uses.—Zinc serves in qualitative analysis for the evolution of hydrogen, and also of arsenetted and antimonetted hydrogen gases (compare § 131, 10, and § 132, 10); it is occasionally used also to precipitate some metals from their solutions; in which process the zinc simply displaces the other metal ($Cu SO_4 + Zn = Zn SO_4 + Cu$). Zinc is also sometimes used for the detection of sulphurous acid and phosphorous acid; it must then be tested for zinc sulphide or zinc phosphide, as the case may be, see §§ 139 and 148.

2. Iron, Fe.

Iron reduces many metals and precipitates them from their solutions in the metallic state. We use it especially for the detection of copper, which precipitates upon it with its characteristic color. Any clean surface of iron, such as a knife-blade, a needle, a piece of wire, etc., will serve for this purpose.

3. Copper, Cu.

We use copper exclusively to effect the reduction of mer-

* According to Gunning (Scheikundige Bijdragen, Deel I. Nr. I, p. 113), the purification may be effected by repeated fusion with a mixture of sodium carbonate and sulphur..

cury, which precipitates upon it as a white coating shining with silvery lustre when rubbed. A copper coin scoured with fine sand, or in fact any clean surface of copper, may be employed for this purpose.

§ 41.

4. Lead Dioxide, PbO_2.

Preparation.—Dissolve separately 4 parts of crystallized lead acetate and 3 parts of crystallized sodium carbonate in hot water, and filter if needful; mix the solutions, and pass well-washed chlorine gas through the mixture until it has become dark brown and all effervescence from escape of carbon dioxide has ceased. Throw on a filter and wash with hot water until silver nitrate no longer causes any turbidity in the washings. The contents of the filter are dried for use. —Wöhler.

Tests.—Lead dioxide, when boiled with thrice its bulk of pure nitric acid for several minutes and allowed to settle, must not communicate the faintest red color to the acid (absence of manganese.)

Uses.—This reagent serves to oxidize chromic oxide when in alkaline solution, to chromic acid. It also is a most delicate and characteristic test for manganese.

§ 42.

5. Bismuthous Hydroxide, Bi O.O H.*

Preparation.—Dissolve bismuth, freed from arsenic by fusion with *hepar sulphuris*, in dilute nitric acid; dilute the solution till a slight permanent precipitate is produced; filter and evaporate the filtrate to crystallization. Wash the crystals with water containing nitric acid, triturate them with water, add ammonia in excess, and let the mixture digest for some time; then filter, wash, and dry the white precipitate, and keep it for use.

Tests.—The bismuth hydroxide is dissolved in dilute nitric

* The basic nitrate of bismuth of commerce, if perfectly free from arsenic and antimony, may also be used instead of the hydroxide.

acid and precipitated with sulphuretted hydrogen. Part of the precipitated sulphide is treated with ammonia and filtered, part is treated with ammonium sulphide and filtered. The filtrates are then mixed with hydrochloric acid in excess; the first should give no precipitate, the second only a white precipitate of sulphur.

Uses.—Bismuth hydroxide when boiled with alkaline solutions of metallic sulphides decomposes with the latter, giving rise to the formation of metallic oxides and bismuth sulphide. It is better adapted to effect decompositions of this kind than cupric oxide, since it enables the operator to judge immediately, upon the addition of a fresh portion, whether the decomposition is complete or not. It has still another advantage over cupric oxide, viz., it does not, like the latter, dissolve in the alkaline fluid in presence of organic substances; nor does it act as a reducing agent upon reducible oxygen compounds. We use it principally to convert arsenious sulphide and arsenic sulphide into arsenious and arsenic acids, for which purpose cupric oxide is altogether inapplicable, since it converts the arsenious acid immediately into arsenic acid, being itself reduced to the state of cuprous oxide.

b. Sulphides.

§ 43.

1. Ammonium Sulphide.

We use in analysis—

a. Colorless ammonium monosulphide. $(NH_4)_2S$.

b. Yellow ammonium polysulphide. $(NH_4)_2S_x$.

Preparation.—a. Transmit hydrogen sulphide through 3 parts of ammonia solution until no further absorption takes place; then add 2 parts more of the same ammonia solution. The action of hydrogen sulphide upon ammonia gives rise to the formation, first, of $(NH_4)_2S$, $[2NH_4OH)$ and $H_2S = (NH_4)_2S$ and $2(H_2O)]$, then of NH_4SH; upon addition of the same quantity of solution of ammonia as has been saturated, the ammonia decomposes with the ammonium hydrosulphide and ammonium monosulphide is formed, thus: $NH_4SH + NH_4OH = (NH_4)_2S + H_2O$. The rule, however, is to add

only two-thirds of the quantity of solution of ammonia, as it is better the preparation should contain a little ammonium hydrosulphide than that free ammonia should be present. To employ ammonium hydrosulphide instead of the simple monosulphide is unnecessary, and tends to increase the smell of sulphuretted hydrogen in the laboratory, as the preparation allows that gas to escape when in contact with metallic acid sulphides.

Ammonium sulphide should be kept in well-corked phials. It is colorless at first, and deposits no sulphur upon addition of acids. Upon exposure to the air, however, it acquires a yellow tint, owing to the formation of ammonium disulphide, which is attended also with formation of ammonia and water, thus: $2(NH_4)_2S + O = (NH_4)_2S_2 + 2NH_3 + H_2O$. Continued action of the oxygen of the air upon the ammonium sulphide tends at first to the formation of still higher sulphides; but afterwards the fluid deposits sulphur, and finally all the ammonium sulphide is decomposed and the solution contains nothing but ammonia and ammonium thiosulphate. The formation of thiosulphate proceeds thus: $(NH_4)_2S_2 + O_3 = (NH_4)_2S_2O_3$.

b. The ammonium sulphide which has turned yellow by moderate exposure to the air may be used for all purposes requiring the employment of yellow ammonium sulphide. The yellow sulphide may also be expeditiously prepared by digesting the monosulphide with some sulphur. All kinds of yellow ammonium sulphide deposit sulphur and look turbid and milky on being mixed with acids.

Tests.—Ammonium sulphide must strongly emit the odor peculiar to it; with acids it must evolve abundance of sulphuretted hydrogen; the evolution of gas may be attended by the separation of a pure white precipitate, but no other precipitate must be formed. Upon evaporation and exposure to a red heat in a platinum dish it must leave no residue. It must not, even on heating, precipitate or render turbid solution of magnesium sulphate or solution of calcium chloride (free ammonia, ammonium carbonate).

Uses.—Ammonium sulphide is one of the most frequently employed reagents. It serves (*a*) to effect the precipitation of those metals which hydrogen sulphide fails to throw down from acid solutions, *e.g.* of iron, cobalt, etc., $(NH_4)_2S + FeSO_4 =$

$FeS + (NH_4)_2SO_4$; (*b*) to separate the metallic sulphides thrown down from acid solutions by hydrogen sulphide, since it dissolves some of them to sulphur salts, as, for instance, the sulphides of arsenic and antimony, etc. $(NH_4)_3AsS_3$, etc., whilst leaving others undissolved—for instance lead sulphide, cadmium sulphide, etc. The ammonium sulphide used for this purpose must contain an excess of sulphur if the metallic sulphides to be dissolved will dissolve only as higher sulphides, as, for instance SnS, which dissolves with ease only as SnS_2.

From solutions of aluminium and chromium salts ammonium sulphide precipitates hydroxides, with escape of sulphuretted hydrogen, as the sulphur compounds corresponding to these hydroxides cannot form in the wet way, $[Al_2(SO_4)_3 + 3(NH_4)_2S + 6H_2O = Al_2(OH)_6 + 3(NH_4)_2SO_4 + 3H_2S]$. Salts insoluble in water are thrown down by ammonium sulphide unaltered from their solutions in acids; thus, for instance, calcium phosphate is precipitated unaltered from its solution in hydrochloric acid.

§ 44.

2. Sodium Sulphide, Na_2S.

Preparation.—Same as ammonium sulphide, except that solution of soda is substituted for solution of ammonia. Filter, if necessary, and keep the fluid obtained in well stoppered bottles. If required to contain some higher sulphide of sodium digest it with powdered sulphur.

Uses.—Sodium sulphide must be substituted for ammonium sulphide to effect the separation of cupric sulphide from sulphur compounds soluble in alkaline sulphides, *e.g.* from stannous sulphide, as cuprous sulphide is not quite insoluble in ammonium sulphide.

V. SALTS.

Of the many salts employed as reagents those of potassium, sodium and ammonium are used principally on account of their acids; salts of sodium may therefore often be substi-

tuted for the corresponding potassium salts, etc. Thus it is almost always a matter of perfect indifference whether we use sodium carbonate or potassium carbonate, potassium ferrocyanide or sodium ferrocyanide, etc. I have therefore here classified the salts of the alkali metals *by their acids*. With the salts of the alkali-earth metals and those of the heavy metals the case is different; these are not used for their acid, but for their base; we may therefore often substitute for one salt of a base another similar one, as *e.g.* barium nitrate or acetate for barium chloride, etc. For this reason I have classified the salts of the alkali-earth metals and of the heavy metals *by their bases*.

a. Salts of the Alkali Metals.

§ 45.

1. Potassium Sulphate, K_2SO_4.*

Preparation.—Purify potassium sulphate of commerce by recrystallization, and dissolve 1 part of the pure salt in 12 parts of water.

Uses.—Potassium sulphate serves to detect and separate barium and strontium. It is in many cases used in preference to dilute sulphuric acid, which is employed for the same purpose, as it does not, like the latter reagent, disturb the neutrality of the solution.

§ 46.

2. Hydrogen Disodium Phosphate, or Sodium Phosphate. $Na_2HPO_4.12H_2O$.†

Preparation.—Purify "phosphate of soda" of commerce by recrystallization, and dissolve 1 part of the pure salt in 10 parts of water for use.

Tests.—Solution of sodium phosphate must not become turbid when heated with ammonia. The precipitates which solution of barium nitrate and solution of silver nitrate pro-

* Or, $SO_2 < \begin{matrix} OK \\ OK \end{matrix}$.

† Or, $PO \begin{matrix} ONa \\ ONa \\ OH \end{matrix} + 12\,H_2O$.

duce in it must completely, and without effervescence, redissolve upon addition of dilute nitric acid.

Uses.—Sodium phosphate precipitates the alkali-earth metals and all the heavy metals from solutions of their salts. It serves in the course of analysis, after the separation of the heavy metals, as a test for alkali-earth metals in general; and, after the separation of barium, strontium and calcium, as a special test for the detection of magnesium; for which latter purpose it is used in conjunction with ammonia, the magnesium precipitating as magnesium ammonium phosphate.

§ 47.

3. Ammonium Oxalate, $(NH_4)_2C_2O_4.2aq.$*

Preparation.—Dissolve commercial oxalic acid to saturation in hot hydrochloric acid of 10 to 12 per cent., cool rapidly with constant agitation, wash the crystals (best with help of a filter pump) with cold water to remove most of the hydrochloric acid, redissolve in hot water, filter hot to separate dirt, cool again with stirring, and wash the crystals with cold water until chlorine is mostly removed.—Stolba.

Dissolve the pure oxalic acid in 2 parts of distilled water, with the aid of heat, add solution of ammonia until the reaction is distinctly alkaline, and put the vessel in a cold place. Let the crystals drain. The mother liquor will, upon proper evaporation, give another crop of crystals. Dissolve 1 part of the pure salt in 24 parts of water for use.

Tests.—The solution of ammonium oxalate must not be precipitated nor rendered turbid by hydrogen sulphide, nor by ammonium sulphide. Ignited on platinum, the salt must volatilize without leaving a residue.

Uses.—Oxalic acid forms with calcium, strontium, barium, lead, and other metals, insoluble or very difficultly soluble compounds; ammonium oxalate produces therefore in the aqueous solutions of the salts of these bases, precipitates of the corresponding oxalates. In analysis it serves principally for the detection and separation of calcium.

* Or, $\begin{matrix} COONH_4 \\ | \\ COONH_4 \end{matrix} + 2H_2O.$

§ 48.

4. Sodium Acetate, $Na\,C_2H_3O_2.3\,aq.$*

Preparation.—Dissolve crystallized sodium carbonate in a little water, add to the solution acetic acid to slight excess, evaporate to crystallization, and purify the salt by recrystallization. This salt is now to be had very pure in commerce. For use dissolve 1 part of the salt in 10 parts of water.

Tests.—Sodium acetate must be colorless and free from empyreumatic matter and inorganic acids.

Uses.—The stronger acids in the free state decompose sodium acetate, combining with the base and setting the acetic acid free. In the course of analysis sodium acetate is used principally to precipitate ferric phosphate (which is insoluble in acetic acid) from its solution in hydrochloric acid. It serves also to effect the separation of ferric oxide and alumina, which it precipitates on boiling from the solutions of their salts.

§ 49.

5. Sodium Carbonate, $(Na_2\,CO_3.10\,aq.)$†

Preparation.—It is best to provide this salt in several grades of purity as follows:

a. For ordinary use as solution select clear, colorless crystals of "sal soda," and dissolve them in twice their weight of water. The solution is likely to contain a little sulphate, chloride, and silicate, and if these are present it must not be used in processes for the detection of the corresponding acids. As sodium carbonate attacks glass, the salt should be kept in the dry state, and dissolved shortly before use.

b. Free from sulphur and chlorine. Finely pulverize "bicarbonate of soda" of commerce, put the powder into a funnel stopped loosely with some cotton, make the surface even, cover it with a disk of thick filter paper with turned-up edges, and wash by pouring small quantities of water on the paper disk until the filtrate, when acidified with nitric acid, is not rendered turbid by solution of silver nitrate, nor by solution

* Or, $\begin{matrix} CH_3 \\ | \\ CO\,ONa \end{matrix} + 3\,H_2O.$ † Or, $CO<\begin{matrix} O\,Na \\ O\,Na \end{matrix} + 10\,H_2O.$

of barium chloride. Let the salt dry, and then convert it by gentle ignition into the simple carbonate. This is effected best in a vessel of silver or platinum; but it may be done also in a perfectly clean iron, or, on a small scale, in a porcelain dish. Dissolve 1 part of the anhydrous salt in 5 parts of water.

[*c. Free from silica.* The salt as prepared in *b*, is liable to contain silica as well as sand and dirt. To purify it further, dissolve in twice its weight of water, or dissolve "sal soda" crystals in their own weight of water, filter, and pass into the cold solution washed and pure carbon dioxide, *but not to complete saturation.*

The crystals of hydrogen sodium carbonate that separate are drained in a funnel, washed with cold water, dried, and gently ignited, as above directed, as long as water is given off. Prepared in glass vessels by this method, sodium carbonate may be readily procured containing but $\frac{1}{10}\frac{1}{00}$ of silica. —EDITOR.

d. To a clear and cold solution of 145 grms. of sal soda crystals in 100 cc. of water, add gradually with vigorous stirring, a solution of 60 grms. of purified oxalic acid (see § 47) in 100 cc. of warm water. When sodium oxalate ceases to separate, break up the crystals, and transfer them to a 6-inch filter connected with the Bunsen filter pump, wash with 500 cc. of water and dry. Heat to full redness in a platinum dish until the oxalate is fully decomposed, dissolve, filter, and evaporate to dryness.—J. LAWRENCE SMITH, private communication.]

Tests.—Sodium carbonate must be perfectly white. Several grammes of the salt must dissolve in water without turbidity, and if the salt is to be used in a flux (see § 78), without leaving grains of sand. Its solution, after supersaturation with nitric acid, must not be rendered turbid by barium chloride or silver nitrate; nor must addition of potassium sulphocyanate impart a red, or warming with ammonium molybdate and nitric acid a yellow tint to it, or give a yellow precipitate; the residue which remains upon evaporating its solution to dryness, after previous supersaturation with hydrochloric acid, must leave no residue (silica) when redissolved in water. When fused in a glass tube with potassium cyanide for a long time in a current of carbon dioxide, it should give no trace of a dark sublimate (arsenic). See § 132, 12.

Uses.—With the exception of the alkali metals, sodium carbonate precipitates all the metals in the form of normal or basic carbonates. Those metals which form soluble acid carbonates require boiling for their complete precipitation from acid solutions. Many of the precipitates produced by the action of sodium carbonate exhibit a characteristic color, which may lead to the detection of the individual metals which they respectively contain. Solution of sodium carbonate serves also for the decomposition of many insoluble salts, more particularly of those with organic acids. Upon boiling with sodium carbonate these salts are converted into insoluble carbonates, whilst the acids combine with the sodium, and are thus obtained in solution. Sodium carbonate is often used also to saturate free acids.

§ 50.

6. Ammonium Carbonate, $(NH_4)_2CO_3$.*

Preparation.—Take commercial "carbonate of ammonia" entirely free from any smell of animal oil, such as is prepared by sublimation, carefully scrape off the outer and inner surface of the mass, and dissolve one part of the salt by digestion with 4 parts of water to which one part of ammonia solution has been added.

Tests.—Pure ammonium carbonate must completely volatilize. Neither solution of barium nitrate nor of silver nitrate, nor hydrogen sulphide, must color or precipitate it, after supersaturation with nitric acid.

Uses.—Ammonium carbonate precipitates, like sodium carbonate, most metals; it is generally employed in preference to the latter reagent, because it introduces no non-volatile body into the solution. Complete precipitation of many of the metals takes place also only on boiling. Several of the precipitates redissolve again in an excess of the precipitant. In like manner ammonium carbonate dissolves many hydroxides and sulphides, and thus enables us to distinguish and separate them from others which are insoluble in this reagent.

Ammonium carbonate, like ammonia solution, and for the same reason, fails to precipitate from acid solutions many

* Or, $CO<^{O\,NH_4}_{O\,NH_4}$.

metals which it precipitates from neutral solutions. (Compare § 53.) We use ammonium carbonate in analysis principally to effect the precipitation of barium, strontium and calcium, and the separation of these substances from magnesium; also to separate arsenious sulphide, which is soluble in it, from antimonious sulphide, which is insoluble.

§ 51.

7. HYDROGEN SODIUM SULPHITE, $HNaSO_3$.*

Preparation.—Heat 5 parts of copper tacks or clippings with 20 parts of concentrated sulphuric acid in a flask, and conduct the sulphur dioxide gas evolved, first through a washing bottle containing some water, then into a flask containing 7 parts of clean crystallized sal soda, and from 20 to 30 parts of water, and which is not much more than half full; continue the transmission of the gas until the evolution of carbon dioxide ceases. Keep the solution, which smells strongly of sulphurous acid, in a well-stoppered bottle.

Tests.—Acid sodium sulphite, when evaporated to dryness with pure sulphuric acid, must leave a residue,† the aqueous solution of which is not altered by hydrogen sulphide, nor precipitated yellow by heating with a solution of ammonium molybdate mixed with nitric acid.

Uses.—Sulphurous acid has a great tendency to pass to the state of sulphuric acid by absorbing oxygen. It is therefore one of our most powerful reducing agents. Acid sulphite of sodium, which has the advantage of being less readily decomposed than sulphurous acid, acts in an analogous manner upon addition of acid. We use it principally to reduce arsenic acid to arsenious acid, chromic acid to chromic oxide, and ferric oxide to ferrous oxide. It will serve also to effect the separation of arsenious sulphide, which is soluble in it, from the sulphides of antimony and tin, which are insoluble in this reagent.

§ 52.

8. POTASSIUM NITRITE, KNO_2.‡

Preparation.—In an iron pan fuse 1 part of nitre, add 2

* Or, $SO{<}^{OH}_{ONa}$.

† The evaporation is attended with copious evolution of sulphur dioxide.

‡ Or, N O–O K.

parts of lead, and keep stirred with an iron rod. Even at a low red heat the lead becomes for the most part oxidized and converted into a yellow powder. To oxidize the remainder, the heat is increased to visible redness and maintained at that point for half an hour. Allow to cool, treat with cold water, filter and pass carbon dioxide through the filtrate. This precipitates almost the whole of the lead in solution, the remainder is removed with a little hydrogen sulphide. Evaporate the clear fluid to dryness, finally with stirring, and fuse in order to destroy any potassium thiosulphate (AUG. STROMEYER). When required, dissolve 1 part in 2 parts of water, neutralize cautiously with acetic acid, and filter.

Tests.—Potassium nitrite must, upon addition of dilute sulphuric acid, copiously evolve nitrogen dioxide gas.

Uses.—Potassium nitrite is an excellent means to effect the detection and separation of cobalt, in the solutions of which metal it produces a precipitate of potassium cobaltic nitrite. It serves also in presence of free acid to liberate iodine from its compounds.

§ 53.

9. POTASSIUM DICHROMATE, $K_2 Cr_2 O_7$.*

Preparation.—Purify "bichromate of potash" by recrystallization, and dissolve one part in 10 parts of water for use.

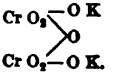
Uses.—Potassium dichromate decomposes most of the soluble metallic salts. Most of the precipitated chromates are very sparingly soluble, and many of them exhibit characteristic colors which lead readily to the detection of the particular metal which they respectively contain. We use potassium dichromate principally as a test for lead.

§ 54.

10. POTASSIUM PYROANTIMONATE,† $H_2 K_2 Sb_2 O_7 . 6H_2O$.‡

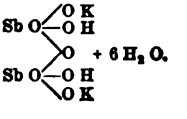
Preparation.—Project a mixture of equal parts of pulver-

* Or,



† Metantimonate of former editions.

‡ Or,



ized tartar-emetic and potassium nitrate in small portions at a time into a red-hot crucible. After the mass has deflagrated, keep it at a moderate red heat for a quarter of an hour; it froths at first, but after some time it will be in a state of calm fusion. Remove the crucible from the fire, let the mass get nearly cold, and extract it with warm water. Transfer to a suitable vessel, by rinsing, and decant the clear fluid from the heavy white powder deposited. Concentrate the decanted fluid by evaporation. After one or two days a doughy mass will separate. Treat this mass with three times its volume of cold water, working it at the same time with a spatula. This operation will serve to convert it into a fine granular powder, to which add the powder from which the fluid was decanted, wash well with boiling water, till the washings cease to be alkaline, and dry on blotting paper. 100 parts of tartar-emetic give about 36 parts of the pyroantimonate (BRUNNER).

Tests and Uses.—Granular potassium antimonate is very sparingly soluble in water, requiring 90 parts of boiling and 250 parts of cold water for solution. The solution is best prepared immediately before use, by boiling the salt with water, and filtering from the undissolved portion. The solution must be clear and of neutral reaction; it must give no precipitate with solution of potassium chloride, nor with solution of ammonium chloride; but solution of sodium chloride must produce a crystalline precipitate in it. Potassium pyroantimonate is a valuable reagent for soda, but its employment requires great caution, see § 90.

§ 55.

11. AMMONIUM MOLYBDATE, $(NH_4)_2MoO_4$, DISSOLVED IN NITRIC ACID.—MOLYBDIC SOLUTION.

Preparation.—Triturate molybdenum sulphide with about an equal bulk of coarse quartz sand washed with hydrochloric acid, until it is reduced to a moderately fine powder; heat to faint redness, with repeated stirring, until the mass has acquired a lemon-yellow color (which after cooling turns whitish). With small quantities this operation may be conducted in a flat platinum dish, with large quantities in a muffle. Extract with solution of ammonia, filter, evaporate the filtrate,

heat the residue to faint redness until it appears yellow or white, and then digest for several days with nitric acid in the water bath, in order to convert any phosphoric acid present to the tribasic state. When the nitric acid is evaporated dissolve the residue in 4 parts of solution of ammonia, filter rapidly, and pour the filtrate into 15 parts by weight of nitric acid of 1.20 specific gravity. Keep the mixture standing several days in a moderately warm place, which will cause the separation of any remaining traces of phosphoric acid as ammonium phosphomolybdate. Decant the colorless fluid from the precipitate and keep it for use. Heated to 40° no white precipitate (molybdic acid or an acid salt of the same) will separate; but above that point precipitation will take place unless more nitric acid be added (EGGERTZ).

Uses.—Phosphoric acid and arsenic acid form with molybdic acid and ammonia peculiar yellow compounds which are almost absolutely insoluble in the nitric acid solution of ammonium molybdate. The phosphoric acid compound is formed in the cold, the arsenic acid compound requires heat. Ammonium molybdate affords therefore an excellent means to detect these acids, and more especially very minute quantities of phosphoric acid in acid solutions containing aluminium and alkali-earth metals.

§ 56.

12. AMMONIUM CHLORIDE, NH_4Cl.

Preparation.—Select sublimed white sal ammoniac of commerce. If it contains iron it must be purified by slowly passing chlorine gas into the nearly saturated solution *for a short time*, or until potassium ferricyanide gives no blue color with a few drops of the liquid. Ammonia is then added in slight excess, the whole is warmed, filtered from the separated ferric oxide, and evaporated to crystallization. Dissolve 1 part of the salt in 8 parts of water for use.

Tests.—Solution of ammonium chloride must leave no fixed residue upon evaporation on platinum. Ammonium sulphide must have no action upon it. Its reaction must be perfectly neutral.

Uses.—Ammonium chloride serves principally to retain in

solution certain oxides (*e.g.*, manganese and magnesium monoxides), or salts (*e.g.*, calcium tartrate), upon the precipitation of other oxides or salts by ammonia or some other reagent. This application of ammonium chloride is based upon the tendency of the ammonium salts to form double compounds with other salts. Ammonium chloride serves also to distinguish between precipitates possessed of similar properties; for instance, to distinguish the magnesium ammonium phosphate, which is insoluble in ammonium chloride, from other magnesian precipitates. It is used also to precipitate from their solutions in potassa various substances which are soluble in that alkali, but insoluble in ammonia; *e.g.*, alumina, chromic oxide, etc. In this process the elements of the ammonium chloride transpose with those of the potassa, and potassium chloride, water, and ammonia are formed. Ammonium chloride is applied also as a special reagent to effect the precipitation of platinum as ammonium platinichloride.

§ 57.

13. Potassium Cyanide, K Cy, or K C N.

Preparation.—Heat potassium ferrocyanide of commerce (perfectly free from potassium sulphate) gently, with stirring, until the crystallization water is completely expelled; triturate the anhydrous mass, and mix 8 parts of the dry powder with 3 parts of perfectly dry potassium carbonate; fuse the mixture in a covered Hessian or, better still, in a covered iron crucible, until the mass is in a faint glow, appears clear, and a sample of it, taken out with a heated glass or iron rod, looks perfectly white. Remove the crucible now from the fire, tap it gently, and let it cool a little until the evolution of gas has ceased; pour the fused potassium cyanide into a heated, tall, crucible-shaped vessel of clean iron or silver, or into a moderately hot Hessian crucible, with proper care to prevent the running out of any of the minute particles of iron which have separated in the process of fusion and have subsided to the bottom of the crucible. Let the mass now slowly cool in a somewhat warm place. The potassium cyanide so prepared is exceedingly well adapted for analytical purposes, although it contains potassium carbonate and cyanate, which

latter is upon solution in water transformed into ammonium carbonate and potassium carbonate [$2C\,N\,O\,K + 4\,H_2\,O = K_2\,C\,O_3 + (N\,H_4)_2\,C\,O_3$]. Keep it in the solid form in a well-stoppered bottle, and dissolve 1 part of it in 4 parts of water, without application of heat, when required for use.

Tests.—Potassium cyanide must be of a milk-white color and quite free from particles of iron or charcoal. It must completely dissolve in water to a clear fluid. It must contain neither silica nor potassium sulphide; the precipitate which lead salts produce in its solution must accordingly be of a white color, and the residue which its solution leaves upon evaporation, after previous supersaturation with hydrochloric acid,* must completely dissolve in water to a clear fluid.

Uses.—Potassium cyanide prepared in the manner described produces in the solutions of most metallic salts precipitates of cyanides of metals or of hydroxides or carbonates which are insoluble in water. The precipitated cyanides are soluble in potassium cyanide, and may therefore by further addition of the reagent be separated from the hydroxides or carbonates which are insoluble in potassium cyanide. Some of the metallic cyanides redissolve invariably in the potassium cyanide as double cyanides, even in the presence of free hydrocyanic acid and upon boiling; whilst others combine with cyanogen to new radicals, which remain in solution in combination with the potassium. The most common compounds of this nature are potassium cobalticyanide and potassium ferro- and ferricyanide.

These differ from the double cyanides of the other kind particularly in this, that dilute acids fail to precipitate the metallic cyanides which they contain. Potassium cyanide may accordingly serve also to separate the metals which form compounds of the latter description from others, the cyanides of which are precipitated by acids from their solution in potassium cyanide. In the course of analysis this reagent is of great importance, as it serves to effect the separation of cobalt from nickel; also that of copper, the sulphide of which metal is soluble in it, from cadmium, whose sulphide is insoluble.

* This supersaturation with hydrochloric acid is attended with disengagement of hydrocyanic acid,

§ 58.

14. Potassium Ferrocyanide, $K_4 Fe Cy_6 + 3$ aq.

Preparation.—The potassium ferrocyanide found in commerce is sufficiently pure. 1 part of the salt is dissolved in 12 parts of water for use.

Uses.—Ferrocyanogen forms with most metals compounds insoluble in water, some of which exhibit highly characteristic colors. These ferrocyanides are formed when potassium ferrocyanide is brought into contact with soluble metallic salts, the potassium changing places with the metals. The cupric and ferric ferrocyanides exhibit the most characteristic colors of all; potassium ferrocyanide serves therefore particularly as a test for cupric and ferric compounds.

§ 59.

15. Potassium Ferricyanide, $K_6 Fe_2 Cy_{12}$.

Preparation.—Conduct chlorine gas slowly into a solution of 1 part of potassium ferrocyanide in 10 parts of water, with frequent stirring, until the solution exhibits a fine deep red color by transmitted light (the light of a candle answers best), and a portion of the fluid produces no longer a blue precipitate in a solution of ferric chloride, but imparts a brownish tint to it. Evaporate the fluid now in a dish to $\frac{1}{4}$ of its weight and let crystallize. The mother liquor will upon further evaporation yield a second crop of crystals equally fit for use as the first. Dissolve the whole of the crystals obtained in 3 parts of water, filter if necessary; evaporate the solution briskly to half its volume, and let crystallize again. The commercial salt may also be employed. The solution, as already remarked, must produce neither a blue precipitate nor a blue color in a solution of ferric chloride. As this salt decomposes when long kept in solution, it is best preserved and applied in the state of powder.

Uses.—Potassium ferricyanide decomposes with solutions of metals in the same manner as potassium ferrocyanide. Of the metallic ferricyanides the ferrous ferricyanide is more particularly characterized by its color, and we apply potassium ferricyanide therefore principally as a test for ferrous compounds.

§ 60.

16. Potassium Sulphocyanate, K C N S.

Preparation.—Mix together 46 parts of anhydrous potassium ferrocyanide, 17 parts of potassium carbonate, and 32 parts of sulphur; introduce the mixture into an iron pan provided with a lid, and fuse over a gentle fire; maintain the same temperature until the swelling of the mass which ensues at first has completely subsided and given place to a state of tranquil and clear fusion; increase the temperature now, towards the end of the operation, to faint redness, in order to decompose the potassium thiosulphate which has been formed in the process. Remove the half refrigerated and still soft mass from the pan, crush it, and boil repeatedly with alcohol of from 80 to 90 per cent. Upon cooling, part of the potassium sulphocyanate will separate in colorless crystals; to obtain the remainder, distil the alcohol from the mother liquor. Dissolve one part of the salt in 10 parts of water for use.

Tests.—Solution of potassium sulphocyanate must remain perfectly colorless when mixed with perfectly pure dilute hydrochloric acid.

Uses.—Potassium sulphocyanate serves for the detection of ferric compounds, for which it is at once the most characteristic and the most delicate test.

b. Salts of the Alkali-Earth Metals.

§ 61.

1. Barium Chloride, $Ba Cl_2 + 2 H_2 O$.

The commercial salt may be used after purification by recrystallizing, if need be.

Preparation.—a. From heavy spar. Mix together 8 parts of pulverized barium sulphate, 2 parts of charcoal in powder, and 1 part of common rosin. Put the mixture in a crucible, and expose it in a wind furnace to a long-continued red heat. Triturate the crude barium sulphide obtained, boil about $\frac{1}{10}$ of the powder with 4 times its quantity of water, and add hydrochloric acid until all effervescence of hydrogen sulphide

has ceased, and the fluid manifests a slight acid reaction. Add now the remaining $\frac{1}{10}$ part of the barium sulphide, boil some time longer, then filter, and let the alkaline fluid crystallize. Drain the crystals, redissolve them in water, and crystallize again.

b. From witherite. Pour 10 parts of water upon 1 part of pulverized witherite, and gradually add crude hydrochloric acid until the witherite is almost completely dissolved. Add now a little more finely pulverized witherite, and heat, with frequent stirring, until the fluid has entirely or very nearly lost its acid reaction; add solution of barium sulphide as long as a precipitate forms; then filter, evaporate the filtrate to crystallization, and purify by crystallizing again. For use, dissolve 1 part of the barium chloride in 10 parts of water.

Tests.—Pure barium chloride must not alter vegetable colors; its solution must not be colored or precipitated by hydrogen sulphide, nor by ammonium sulphide. Pure sulphuric acid must precipitate every fixed particle from it, so that the fluid filtered from the precipitate formed upon the addition of that reagent leaves not the slightest residue when evaporated on platinum foil.

Uses.—Barium forms with many acids soluble, with others insoluble compounds. This property of barium affords us therefore a means of distinguishing the former acids, which are not precipitated by barium chloride, from the latter, in the solution of the salts of which this reagent produces a precipitate. The precipitated barium salts severally show with acids a different deportment. By subjecting these salts to the action of acids we are therefore enabled to subdivide the group of precipitable acids and even to detect certain individual acids. This makes barium chloride one of our most important reagents to distinguish between certain groups of acids, and more especially also to effect the detection of sulphuric acid.

§ 62.

2. Barium Nitrate, $Ba(NO_3)_2$*.

Preparation.—Treat barium carbonate, no matter whether

* Or, $\begin{matrix} N\,O_2\,O \\ N\,O_2\,O \end{matrix} > Ba$.

witherite or that precipitated by sodium carbonate from solution of barium sulphide, with dilute nitric acid free from chlorine, and proceed exactly as directed in the preparation of barium chloride from witherite, or else recrystallize the commercial salt. For use, dissolve 1 part of the salt in 15 parts of water.

Tests.—Solution of barium nitrate must not be made turbid by solution of silver nitrate. Other tests are the same as for barium chloride.

Uses.—Barium nitrate is used instead of barium chloride in cases where it is desirable to avoid the presence of a metallic chloride in the fluid.

§ 63.

3. Barium Carbonate, $BaCO_3$.*

Preparation.—Dissolve crystallized barium chloride in water, heat to boiling, and add a solution of ammonium carbonate mixed with some caustic ammonia, or of pure sodium carbonate, as long as a precipitate forms; let the precipitate subside, decant five or six times, transfer the precipitate to a filter, and wash until the washing water is no longer rendered turbid by solution of silver nitrate. Stir the precipitate with water to the consistence of thick milk, and keep this mixture in a stoppered bottle. It must of course be shaken every time it is required for use.

Test.—Pure sulphuric acid must precipitate every fixed particle from a solution of barium carbonate in hydrochloric acid (compare § 38).

Uses.—Barium carbonate completely decomposes the solutions of certain metallic salts, precipitating from them the whole of the metal as hydroxide and basic salt, whilst some other metallic salts are not precipitated by it. It serves therefore to separate the former from the latter, and affords an excellent means of effecting the separation of ferric oxide and alumina from the monoxides of manganese, zinc, calcium, magnesium, etc. It must be borne in mind, however, that the salts must not be sulphates, as barium carbonate equally precipitates the latter bases from these compounds.

* $CO<^{O}_{O}>Ba$.

§ 64.

4. CALCIUM SULPHATE, $CaSO_4$,* *crystallized* + $2H_2O$.

Preparation.—Digest and shake powdered crystallized gypsum (selenite) for some time with water; let the undissolved portion subside, decant, and keep the clear fluid for use.

Uses.—Calcium sulphate, being difficultly soluble, is a convenient agent in cases where it is wished to apply a solution of a calcium salt or of a sulphate of a definite degree of dilution. As dilute solution of a calcium salt it is used for the detection of oxalic acid; whilst as dilute solution of a sulphate it affords an excellent means of distinguishing between barium, strontium and calcium.

§ 65.

5. CALCIUM CHLORIDE, $CaCl_2$, *crystallized* + $6H_2O$.

Preparation.—Dilute 1 part of crude hydrochloric acid with 6 parts of water, and add thereto marble or chalk until the last portion added remains undissolved; add now some slacked lime, then hydrogen sulphide until a filtered portion of the mixture is no longer altered by ammonium sulphide. Then let the mixture stand covered for 12 hours at a gentle heat; filter, exactly neutralize the filtrate, concentrate by evaporation, and crystallize. Let the crystals drain, and dissolve 1 part of the salt in 5 parts of water for use.

Tests.—Solution of calcium chloride must be perfectly neutral, and neither be colored nor precipitated by ammonium sulphide; nor ought it to evolve ammonia when mixed with potassa or lime.

Uses.—Calcium chloride is in its action and application analogous to barium chloride. For as the latter reagent is used to separate the inorganic acids into groups, so calcium chloride serves in the same manner to effect the separation of the organic acids into groups, since it precipitates some of them, whilst it forms soluble compounds with others. And, as is the case with the barium precipitates, the different conditions under which the various insoluble calcium salts are thrown down enable us to subdivide the group of precipitable acids.

*$SO_2 <^{O}_{O}> Ca$.

§ 66.

6. MAGNESIUM SULPHATE, $Mg\,S\,O_4$, *crystallized* + $7H_2O$.

Preparation.—Dissolve 1 part of magnesium sulphate of commerce in 10 parts of water; if the salt is not perfectly pure, subject it to recrystallization.

Tests.—Magnesium sulphate must have a neutral reaction. Its solution, when mixed with a sufficient quantity of ammonium chloride must, after the lapse of half an hour, not appear clouded or tinged by ammonia, or by ammonium carbonate or oxalate or sulphide.

Uses.—Magnesium sulphate serves almost exclusively for the detection of phosphoric acid and arsenic acid, which it precipitates from aqueous solutions of phosphates and arsenates, in presence of ammonia and ammonium chloride, in the form of almost absolutely insoluble highly characteristic salts (ammonium magnesium phosphate or arsenate). Magnesium sulphate is also employed to test ammonium sulphide (see § 43).

c. SALTS OF THE HEAVY METALS.

§ 67.

1. FERROUS SULPHATE, $Fe\,S\,O_4$* *crystallized* + $7H_2O$.

Preparation.—Heat an excess of iron nails free from rust, or of clean iron wire, with dilute sulphuric acid until the evolution of hydrogen ceases; filter the sufficiently concentrated solution, add a few drops of dilute sulphuric acid to the filtrate, and allow it to cool. Wash the crystals with water very slightly acidulated with sulphuric acid, dry, and keep for use. The commercial "protosulphate of iron" sold for photographic use answers every purpose of analytical chemistry.

Tests.—The crystals of ferrous sulphate must have a fine pale green color. Crystals that have been more or less oxidized by the action of the air, and give a brownish-yellow solution when treated with water, leaving undissolved ferric sulphate behind, must be altogether rejected. Hydrogen sulphide must not precipitate solution of ferrous sulphate

* Or, $SO_2{<}^{O}_{O}{>}Fe$.

after addition of some hydrochloric acid, nor even impart a blackish tint to it.

Uses.—Ferrous sulphate has a great disposition to absorb oxygen, and to be converted into ferric sulphate. It acts therefore as a powerful reducing agent. We employ it principally for the reduction of nitric acid, from which* it separates nitrosyl (2NO) by withdrawing three atoms of oxygen from it. The decomposition of the nitric acid being attended in this case with the formation of a very peculiar brownish-black compound of nitrosyl (p. 270), with an undecomposed portion of the ferrous salt, this reaction affords a particularly characteristic and delicate test for the detection of nitric acid. Ferrous sulphate serves also for the detection of ferricyanides, with which it produces a kind of Prussian blue, and also to effect the precipitation of metallic gold from solutions of that metal.

§ 68.

2. Ferric Chloride, Fe_2Cl_6.†

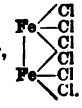
Preparation.—Heat in a flask a mixture of 10 parts of water and 1 part of pure hydrochloric acid with small iron nails until no further evolution of hydrogen is observed, even after adding the nails in excess; filter the solution into another flask, and conduct into it chlorine gas, with frequent shaking, until the fluid no longer produces a blue precipitate in solution of potassium ferricyanide. Heat until the excess of chlorine is expelled. Dilute until the fluid is twenty times the weight of the iron dissolved, and keep for use.

Tests.—Solution of ferric chloride must not contain an excess of acid; this may be readily ascertained by stirring a diluted sample of it with a glass rod dipped in ammonia, when the absence of any excess of acid will be proved by the formation of a precipitate which shaking the vessel or agitating the fluid fails to redissolve. Potassium ferricyanide must not impart a blue color to it.

Uses.—Ferric chloride serves to subdivide the group of

* Considered as N_2O_4. Sec § 159, 6.

† Or,



organic acids which calcium chloride fails to precipitate, as it produces precipitates in solutions of benzoates and succinates, but not in cold solutions of acetates and formates. The aqueous solutions of normal ferric acetate and formate exhibit an intensely red color; ferric chloride is therefore a useful agent for detecting acetic acid and formic acid. Ferric chloride is exceedingly well adapted to effect the decomposition of phosphates of the alkali-earth metals (see § 142). It serves also for the detection of ferrocyanides, with which it produces Prussian blue.

§ 69.

3. Silver Nitrate, $AgNO_3$.*

Preparation.—Dissolve 1 part of the pure crystallized salt in 20 parts of water.

Tests.—Dilute hydrochloric acid must completely precipitate all fixed particles from solution of silver nitrate, which should have a neutral reaction; the fluid filtered from the precipitated silver chloride must accordingly leave no residue when evaporated on a watch-glass, and must be neither precipitated nor colored by hydrogen sulphide.

Uses.—Silver forms with many acids soluble, with others insoluble compounds. Silver nitrate may therefore serve, like barium chloride, to effect the separation and arrangement of acids into groups.

Most of the insoluble compounds of silver dissolve in dilute nitric acid; chloride, bromide, iodide and cyanide, ferrocyanide, ferricyanide and sulphide of silver are insoluble in that menstruum. Silver nitrate is therefore a most excellent agent to distinguish and separate from all other acids the acids corresponding to the last enumerated compounds of silver. Many of the insoluble salts of silver exhibit a peculiar color (silver chromate, silver arsenate) or manifest a characteristic deportment with other reagents or upon the application of heat (silver formate); silver nitrate is therefore an important agent for the positive detection of certain acids.

* Or, NO_2–O Ag.

§ 70.

4. LEAD ACETATE, $Pb(C_2H_3O_2)_2$,* *crystallized* + $3H_2O$.

The best lead acetate of commerce is sufficiently pure; for use dissolve 1 part of the salt in 10 parts of water.

Tests.—Lead acetate must completely dissolve in water acidified with one or two drops of acetic acid; the solution must be quite clear and colorless; hydrogen sulphide must throw down all fixed particles from it. On mixing the solution with ammonium carbonate in excess, and filtering, the filtrate must not show a bluish tint (copper).

Uses.—Lead forms with a great many acids compounds insoluble in water, which are marked either by peculiarity of color or characteristic deportment. Lead acetate therefore produces precipitates in the solutions of these acids or of their salts, and serves for the detection of several of them. Thus lead chromate is characterized by its yellow color, lead phosphate by its peculiar deportment before the blowpipe, and lead malate by its ready fusibility.

§ 71.

5. MERCUROUS NITRATE, $Hg_2(NO_3)_2$,† *crystallized* + $2H_2O$.

Preparation.—Pour 1 part of pure nitric acid of 1.2 spec. gr. on 1 part of pure mercury in a porcelain dish, and let the vessel stand twenty-four hours in a cool place; separate the crystals formed from the undissolved mercury and the mother liquor, and dissolve them in water mixed with one-sixteenth part of nitric acid, by trituration in a mortar. Filter the solution, and keep the filtrate in a bottle with some metallic mercury covering the bottom of the vessel.

Tests.—The solution of mercurous nitrate must give with dilute hydrochloric acid a copious white precipitate of mercurous chloride; hydrogen sulphide must produce no precipitate in the fluid filtered from this, or at all events only a trifling black precipitate (mercuric sulphide).

* Or, $\begin{matrix} H_3C\text{-}COO \\ H_3C\text{-}COO \end{matrix}\!>\!Pb$.

† Or, $\begin{matrix} NO_3\text{-}O\,Hg \\ | \\ NO_3\text{-}O\,Hg \end{matrix}$.

Uses.—Mercurous nitrate acts in an analogous manner to the corresponding silver salt. In the first place, it precipitates many acids, and, in the second place, it serves for the detection of several readily oxidizable bodies, *e.g.*, of formic acid, as the oxidation of such bodies, which takes place at the expense of the oxygen of the mercurous salt, is attended with the highly characteristic separation of metallic mercury.

§ 72.

6. Mercuric Chloride, $HgCl_2$.

The corrosive sublimate of commerce is sufficiently pure. For use dissolve 1 part of salt in 16 parts of water.

Uses.—Mercuric chloride gives with several acids, *e.g.*, with hydriodic acid, peculiarly colored precipitates, and may accordingly be used for the detection of these acids. It is an important agent for the detection of tin, where that metal is in solution in the state of stannous chloride; if only the smallest quantity of that compound is present, the addition of mercuric chloride in excess to the solution is followed by separation of mercurous chloride insoluble in water. In a similar manner mercuric chloride serves also for the detection of formic acid.

§ 73.

7. Copper Sulphate, or Cupric Sulphate, $CuSO_4$*, *crystallized* + $5H_2O$.

Preparation.—This reagent may be obtained in a state of great purity from the residue remaining in the flask in the process of preparing hydrogen sodium sulphite (§ 51), by treating with water, applying heat, filtering, adding a few drops of nitric acid, boiling for some time, allowing to crystallize, and purifying the salt by recrystallization. For use dissolve 1 part in 10 parts of water.

Tests.—After precipitation by hydrogen sulphide, ammonia and ammonium sulphide must leave the filtrate unaltered.

* Or, $SO_2{<}^{O}_{O}{>}Cu$.

Uses.—Copper sulphate is employed in qualitative analysis to effect the precipitation of hydriodic acid in the form of cuprous iodide. For this purpose it is necessary to mix the solution of one part of copper sulphate with 2½ parts of ferrous sulphate, otherwise half of the iodine will separate in the free state. The ferrous salt changes in this process to ferric salt, at the expense of the cupric sulphate, which latter is thus reduced to cuprous salt;* copper sulphate is used also for the detection of arsenious and arsenic acids; it serves likewise as a test for the soluble ferrocyanides.

§ 74.

8. Stannous Chloride, $Sn Cl_2$, *crystallized* + $2H_2O$.

Preparation.—Reduce grain tin to powder by means of a file, or by fusing it in a small porcelain dish, removing from the fire, and triturating with a pestle until it has passed again to the solid state. Boil the powder for some time with concentrated hydrochloric acid and a few drops of hydrochloroplatinic acid in a flask (taking care always to have an excess of tin in the vessel) until hydrogen gas is scarcely evolved; dilute the solution with 4 times the quantity of water slightly acidulated with hydrochloric acid, and filter. Keep the filtrate for use in a well-stoppered bottle containing small pieces of metallic tin, or some pure tin-foil. If these precautions are neglected the stannous chloride will soon change to stannic chloride, with separation of white oxychloride, which will render the reagent unfit for use.

Tests.—Solution of stannous chloride must, when added to excess of solution of mercuric chloride, immediately produce a white precipitate of mercurous chloride; when treated with hydrogen sulphide it must give a dark brown precipitate; it must not be precipitated nor rendered turbid by sulphuric acid.

Uses.—The great tendency of stannous chloride to absorb oxygen, and thus to form stannic oxide, or rather stannic chloride, as the stannic oxide at the moment of its formation decomposes with the free hydrochloric acid present—makes

* $(Fe S O_4)_2 + (Cu S O_4)_2 = Fe_2 (S O_4)_3 + Cu_2 S O_4$.

this substance one of our most powerful reducing agents. It is more particularly suited to withdraw part or the whole of the chlorine from chlorides. We employ it in the course of analysis as a test for mercury; also to effect the detection of gold.

§ 75.

9. HYDROCHLOROPLATINIC ACID,* H_2PtCl_6, *crystallized* + $6H_2O$.

Preparation.—Heat in a clay crucible 5 parts of zinc to fusion, with sufficient common salt to cover the surface and prevent its oxidation, then introduce 1 part of platinum scraps in small quantities at a time into the fused metal. An alloy is formed from which the zinc is to be removed by digesting in somewhat dilute common hydrochloric acid, until all effervescence ceases, and subsequent boiling for a time with fresh hydrochloric acid. The residual platinum is completely washed with water and boiled with nitric acid. It is again washed, and finally dissolved by warming with concentrated hydrochloric acid and some nitric acid. Evaporate the solution on the water-bath, with addition of hydrochloric acid, and dissolve the semifluid residue in 10 parts of water for use.

Tests.—Hydrochloroplatinic acid must, upon evaporation to dryness in the water-bath, leave a residue which dissolves completely in alcohol.

Uses.—Hydrochloroplatinic acid forms very sparingly soluble salts with potassium and ammonium (also with cæsium and rubidium), but a very soluble salt with sodium; it serves therefore for discriminating the alkali metals.

§ 76.

10. SODIUM PALLADICHLORIDE, Na_2PdCl_4.†

Dissolve 5 parts of palladium in nitrohydrochloric acid, add 6 parts of pure sodium chloride, evaporate in the water-bath to dryness, and dissolve 1 part of the residuary salt in 12 parts of water for use. The brownish solution affords an excellent means for detecting and separating iodine.

* Platinic chloride of the last edition.
† Sodium palladio-chloride of the last edition.

§ 77.

11. Hydrochlorauric Acid,* H Au Cl_4.

Preparation.—Take fine shreds of gold, which may be alloyed with silver or copper, treat them in a flask with nitrohydrochloric acid in excess, and apply a gentle heat until no more of the metal dissolves, then dilute the solution with 10 parts of water. If the gold was alloyed with copper—which is known by the brownish-red precipitate produced by potassium ferrocyanide in a portion of the solution diluted with water—mix it with solution of ferrous sulphate in excess. This will reduce the hydrochlorauric acid to metallic gold, which will separate in the form of a fine brownish-black powder; wash the powder in a small flask, and redissolve it in nitrohydrochloric acid; evaporate the solution on the water-bath, and dissolve the residue in 30 parts of water. If the gold was alloyed with silver, the latter metal remains as chloride upon treating the alloy with nitrohydrochloric acid. In that case evaporate the solution at once, and dissolve the residue in water for use.

Uses.—Hydrochlorauric acid has a great tendency to yield up its chlorine; it therefore readily converts lower chlorides into higher chlorides, and lower oxides, with the co-operation of water, into higher oxides. These chloridations or oxidations are usually indicated by the precipitation of pure metallic gold in the form of a brownish-black powder. In the course of analysis this reagent is used only for the detection of stannous salts, in the solutions of which it produces a brownish-red or purple color or precipitate.

B. REAGENTS IN THE DRY WAY.

I. Fluxes and Decomposing Agents.

§ 78.

1. Sodium Carbonate, Na_2CO_3.

Preparation and *tests* as in § 49, *b*, *c*, and *d*.

Uses.—If silicic oxide or a silicate is fused with about 4

* Auric chloride, or gold trichloride of the last edition.

parts (consequently with an excess) of sodium carbonate, carbonic gas escapes with effervescence, and a basic alkali-silicate is formed, which, being soluble in water, may be readily separated from such metallic oxides as it may contain in admixture; from this basic alkali-silicate hydrochloric acid separates the silicic acid. For this fusion, if traces of silica are to be looked for, the flux must be prepared as given § 46, *c*, or *d*. If sodium carbonate is fused together with sulphates of barium, strontium, or calcium, there are formed carbonates of the alkali-earth metals and sodium sulphate, in which new compounds both the base and the acid of the originally insoluble salt may now be readily detected. For this fusion use the sodium carbonate made as directed § 46 *b*. The fusion with alkali carbonates is invariably effected in a platinum crucible, provided no reducible metallic compound be present.

§ 79.

2. Calcium Carbonate, $Ca\,C\,O_3$.*

Preparation.—Solution of pure calcium chloride, § 65, is heated to boiling and precipitated by a slight excess of solution of ammonium carbonate with addition of some ammonia, § 50. The precipitate is washed five or six times with hot water by decantation, then is brought upon a filter and further edulcorated until the washings give no turbidity with silver nitrate. The contents of the filter are then dried and bottled.

Tests.—Calcium carbonate for use as a flux must be free from salts of the fixed alkalies. When washed with hot water the washing must yield no residue when evaporated to dryness. For uses, see ammonium chloride, § 80.

§ 80.

3. Ammonium Chloride, $N\,H_4\,Cl$.

Preparation.—Crystals of ammonium chloride, prepared as described in § 56, are dried and preserved in a wide-mouthed bottle.

Tests.—Ammonium chloride must be free from salts of the

*Or, $CO<^{O}_{O}>Ca$.

alkali metals. A considerable quantity, when ignited in a platinum vessel, must leave no residue.

Uses.—When a silicate containing alkali metals, that is insoluble in acids, is intimately mixed in a state of fine powder with ammonium chloride and calcium carbonate in suitable proportions, and heated for some time in a platinum crucible, a mass results, from which hot water extracts, besides caustic lime and calcium chloride, the alkalies of the silicate in the form of chlorides, while the silica and other bases remain behind undissolved. Ammonium carbonate (or oxalate) may be used to remove the lime from the solution, and the filtrate, on evaporation to dryness and ignition, yields the alkali metals as pure chlorides (or carbonates). In this operation the larger share of the calcium carbonate, at a red heat, loses carbonic gas and is converted into caustic lime. A smaller portion, by the action of ammonium chloride, is converted into calcium chloride, which, readily fusing, allows the lime and silicate to come into intimate contact, whereby insoluble basic calcium silicate, and soluble alkali chlorides result.—(*J. Lawrence Smith.*) This is incomparably the best method of fluxing silicates for the separation of the alkali metals. See § 210, 2, *c.*

§ 81.

4. Sodium Nitrate, $NaNO_3$ or $NaO . NO_5$.

Preparation.—Neutralize pure nitric acid with pure sodium carbonate exactly, and evaporate to crystallization. Dry the crystals thoroughly, triturate, and keep the powder for use.

Tests.—A solution of sodium nitrate must not be made turbid by solution of silver nitrate or barium nitrate, nor precipitated by sodium carbonate.

Uses.—Sodium nitrate serves as a very powerful oxidizing agent, by yielding oxygen to combustible substances when heated with them. We use this reagent principally to convert several metallic sulphides, and more particularly the sulphides of tin, antimony, and arsenic into oxides or acids; also to effect the rapid and complete combustion of organic substances. For the latter purpose, however, ammonium nitrate is sometimes preferable; it is prepared by saturating nitric acid with ammonium carbonate.

§ 82.

5. Sodium Disulphate, $K_2S_2O_7$.*

Preparation.—Mix 7 parts of pure sodium sulphate (obtained by recrystallization of clean Glauber's salts, and drying away the water of crystallization at a gentle heat), with 5 parts of pure concentrated sulphuric acid, in a platinum dish or large platinum crucible, heat to low redness till the mass is in a state of calm fusion, then pour out into a platinum dish placed in cold water, or upon a piece of porcelain, break the cake into smaller pieces and keep for use.

Tests.—The sodium disulphate must dissolve in water with ease to a clear fluid with a strong acid reaction. The solution must not be rendered turbid or precipitated by hydrogen sulphide or by ammonia and ammonium sulphide.

Uses.—The sodium disulphate at the temperature of fusion dissolves and decomposes many bodies which cannot be dissolved and decomposed by acids in the wet way without considerable difficulty, such as ignited alumina, titanic oxide, chrome ironstone, &c. This reagent, therefore, is of service in effecting the solution or decomposition of such bodies. The fusion is preferably effected in platinum vessels.

II. Blowpipe Reagents.

§ 83.

1. Sodium Carbonate, Na_2CO_3 or NaO^-CO^-ONa.

Preparation.—See § 49.

Uses.—Sodium carbonate serves, in the first place, to promote the reduction of oxidized substances in the inner flame of the blowpipe. In fusing it brings the oxides into the most intimate contact with the charcoal support, and enables the flame to embrace every part of the substance under examination. With salts of the heavy metals the reduction is preceded by separation of the base. It co-operates in this process also chemically by the transposition of its constitu-

* Or, $\begin{matrix} KOSO_2 \\ KOSO_2 \end{matrix}\!\!>\!O$.

ents (according to R. WAGNER, in consequence of the formation of sodium cyanide). Where the quantity operated upon was very minute, the reduced metal is often found in the pores of the charcoal. In such cases the parts surrounding the cavity which contained the substance are dug out with a knife, and triturated in a small mortar; the charcoal is then washed off from the metallic particles, which now become visible either in the form of powder or as small spangles, as the case may be.

Sodium carbonate serves, in the second place, as a solvent. Platinum wire is the most convenient support for testing the solubility of substances in fusing sodium carbonate. A few only of the bases dissolve in fusing sodium carbonate, but acids dissolve in it with facility. Sodium carbonate is also applied as a decomposing agent and a flux, and more particularly to effect the decomposition of the insoluble sulphates, with which it exchanges acids, the newly formed sodium sulphate being reduced at the same time to sodium sulphide; and to effect the decomposition of arsenious sulphide, with which it forms a double arsenious and sodium sulphide, and sodium arsenite or arsenate, thus converting it to a state which permits its subsequent reduction by hydrogen. Sodium carbonate also is the most sensitive reagent in the dry way for the detection of manganese, as it produces when fused in the outer flame with a substance containing manganese a green opaque bead, owing to the formation of sodium manganate.

§ 84.

2. POTASSIUM CYANIDE, K Cy.

Preparation.—See § 57.

Uses.—Potassium cyanide is an exceedingly powerful reducing agent in the dry way; indeed it excels in its action almost all other reagents of the same class, and separates the metals not only from most oxygen compounds, but also from many sulphur compounds. This reduction is attended in the former case with formation of potassium cyanate, by the absorption of oxygen, and in the latter case with formation of potassium sulphocyanate, by the taking up of sulphur. By means of this reagent we may effect the reduction of metals

from their compounds with the greatest possible facility; thus we may, for instance, produce metallic antimony from antimonious acid or from antimony sulphides, metallic iron from ferric oxide, etc. The readiness with which potassium cyanide enters into fusion facilitates the reduction of the metals greatly; the process may usually be conducted even in a porcelain crucible over a spirit or gas lamp. Potassium cyanide is a most valuable and important agent to effect the reduction of stannic oxide, antimonic oxide, and more particularly of arsenious sulphide. Potassium cyanide is equally important as a blowpipe reagent. Its action is exceedingly energetic; substances like stannic oxide, the reduction of which by means of sodium carbonate requires a tolerably strong flame, are reduced by potassium cyanide with the greatest facility. In blowpipe experiments we invariably use a mixture of equal parts of sodium carbonate and potassium cyanide; the admixture of the former is intended here to check in some measure the excessive fusibility of the potassium cyanide. This mixture, besides being a far more powerful reducing agent than the simple sodium carbonate, has, moreover, this great advantage over the latter, that it is absorbed by the pores of the charcoal with extreme facility, and thus permits the production of the metallic globules in a state of the greatest purity.

§ 85.

3. Sodium Tetraborate. *Borax.*

$(Na_2 B_4 O_7$ *), *crystallized* + $10H_2 O$.

The purity of commercial borax may be tested by adding to its solution sodium carbonate, or, after previous addition of nitric acid, solution of barium nitrate or of silver nitrate. The borax may be considered pure if these reagents fail to produce any alteration in the solution; but if either of them causes the formation of a precipitate, or renders the fluid turbid, recrystallization is necessary. The pure crystallized borax is exposed to a gentle heat, in a platinum crucible

* Or, $O{=}B{-}O{-}B{<}^{O\,Na.}_{O\,Na.}$

until it ceases to swell; it is then left to cool, and afterwards pulverized and kept for use.

Borax in a state of fusion decomposes metallic salts and dissolves metallic oxides with formation of characteristically colored glasses, which makes it one of the most valuable of reagents. In the process of fusing with borax we usually select platinum wire for a support; the loop of the wire is moistened or heated to redness, then dipped into the powder and exposed to the outer flame; a colorless bead of fused borax is thus produced. A small portion of the substance is then attached to the bead, by bringing the latter into contact with it whilst still hot or having previously moistened it. The bead with the substance adhering is now exposed to the gas or blowpipe flame, and the reactions are observed. The following points ought to be more particularly watched:—(1) Whether or not the substance dissolves to a transparent bead, and whether or not the bead retains its transparency on cooling; (2) whether the bead exhibits a distinct color, which in many cases at once clearly indicates the individual metal which the substance contains, as is the case, for instance with cobalt: and (3) whether the bead manifests the same or a different deportment in the outer and in the inner flame. Reactions of the latter kind arise from the ensuing reduction of higher to lower oxides, or even to the metallic state, and are for some substances particularly characteristic.

§ 85 *a*.

4. HYDROGEN SODIUM AMMONIUM PHOSPHATE. *Microcosmic Salt, Salt of Phosphorus.*

$(HNa\,NH_4)\,PO_4$,* *crystallized* + $8H_2O$,

and SODIUM METAPHOSPHATE, $NaPO_3$.

Preparation.—a. Heat to boiling 6 parts of hydrogen disodium phosphate and 1 part of pure ammonium chloride with 2 parts of water, and let the solution cool. Free the crys-

* Or, $PO\begin{cases} OH \\ O\,Na \\ O\,NH_4 \end{cases}$

tals produced from the sodium chloride which adheres to them, by recrystallization, with addition of some solution of ammonia. Dry the purified crystals, pulverize and keep for use.

b. Take 2 equal parts of pure tribasic phosphoric acid, and add solution of soda to the one, solution of ammonia to the other, until both fluids have a distinct alkaline reaction; mix the two together, and let the mixture crystallize.

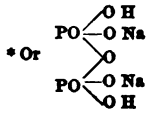
Tests.—Hydrogen sodium ammonium phosphate dissolves in water to a fluid with feebly alkaline reaction. The yellow precipitate produced in this fluid by silver nitrate must completely dissolve in nitric acid. Upon fusion on a platinum wire, microcosmic salt must give a clear and colorless bead.

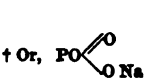
Uses.—On heating two molecules of hydrogen sodium ammonium phosphate, a molecule of water and one of ammonia escape, together with the water of crystallization, leaving hydrogen sodium pyrophosphate $H_2 Na_2 P_2 O_7$; * upon heating more strongly an additional molecule of water escapes, and two molecules of readily fusible *sodium metaphosphate*, $Na PO_3$, † are left behind. The action of sodium metaphosphate is quite analogous to that of sodium tetraborate. We prefer it, however, in some cases to borax as a solvent or flux, the beads which it forms with many substances being more distinctly colored than those of borax. Platinum wire is also used for a support in the process of fluxing with sodium metaphosphate; the loop must be made small and narrow, otherwise the bead will not adhere to it. The operation is conducted as directed in the preceding paragraph.

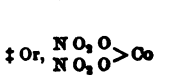
§ 85 *b.*

5. Cobalt Nitrate. $Co (N O_3)_2$, ‡ *crystallized* + $5 H_2 O$.

Preparation.—Fuse in an Hessian crucible 3 parts of potassium disulphate, and add to the fused mass, in small portions at a time, 1 part of well-roasted cobalt ore (the purest zaffre you can procure) reduced to fine powder. The mass thickens







and acquires a pasty consistence. Heat now more strongly until it has become more fluid again, and continue to apply heat until the excess of sulphuric acid is *completely* expelled, and the mass accordingly no longer emits white fumes. Remove the fused mass now from the crucible with an iron spoon or spatula, let it cool, and reduce it to powder; boil this with water until the undissolved portion presents a soft mass; then filter the rose-red solution, which is free from arsenic and nickel, and mostly also from iron. Add to the filtrate a small quantity of sodium carbonate, so as to throw down a little cobalt carbonate, boil, and filter. Precipitate the solution which is now free from iron, boiling with sodium carbonate, wash the precipitate well, and treat it still moist with oxalic acid in excess. Wash the rose-red cobalt oxalate thoroughly, dry, and heat to redness in a glass tube, in a current of hydrogen gas. This decomposes the oxalate into carbonic gas, which escapes, and metallic cobalt which is left behind. Wash the metal, first with water containing acetic acid, then with pure water, dissolve in dilute nitric acid, treat, if necessary, with hydrogen sulphide, filter the fluid from the copper sulphide, &c., which may precipitate, evaporate the solution in the water-bath to dryness, and dissolve 1 part of the residue in 10 parts of water for use.

Tests.—Solution of cobalt nitrate must be free from other metals, and especially also from salts of the alkali metals; when precipitated with ammonium sulphide and filtered, the filtrate must upon evaporation on platinum leave no fixed residue.

Uses.—Cobalt monoxide forms upon ignition with certain infusible bodies (zinc oxide, alumina) peculiarly colored compounds, and may accordingly serve for their detection.

SECTION III.

REACTIONS, OR DEPORTMENT OF BODIES WITH REAGENTS.

§ 86.

I STATED in my introductory remarks that the operations and experiments of qualitative analysis have for their object

the conversion of the unknown constituents of any given compound into forms of which we know the deportment, relations, and properties, and which will accordingly permit us to draw correct inferences regarding the several constituents of which the analyzed compound consists. The greater or less value of such analytical experiments, like that of all other inquiries and investigations, depends upon the greater or less degree of certainty with which they lead to definite results, no matter whether of a positive or negative nature. But as a question does not render us any the wiser if we do not know the language in which the answer is returned, so in like manner will analytical investigations prove unavailing if we do not understand the mode of expression in which the desired information is conveyed to us; in other words, if we do not know how to interpret the phenomena produced by the action of our reagents upon the substance examined.

Before we can therefore proceed to enter upon the practical investigation of analytical chemistry, it is indispensable that we should really possess the most perfect knowledge of the deportment, relations, and properties of the new forms into which we intend to convert the substances we wish to analyze. Now this perfect knowledge consists, in the first place, in a clear conception and comprehension of the conditions necessary for the formation of the new compounds and the manifestation of the various reactions; and in the second place, in a distinct impression of the color, form, and physical properties which characterize the new compound. This section of the work demands therefore not only the most careful and attentive study, but requires, moreover, that the student should *examine, and, as far as possible, verify by actual experiment every fact asserted in it.*

I have, in the present work, arranged those substances which are in many respects analogous, into groups, thus, by comparing their analogies with their differences, to place the latter in the clearest possible light.

A.—Deportment of the Metallic mostly Basic Radicals.

§ 87.

Before proceeding to the special study of the several metals, I give here a general view of the whole of them classified in

groups, showing which belong to each group. The grounds upon which the classification has been arranged will appear from the special consideration of the several groups.

First group—

Potassium, sodium, ammonium (cæsium, rubidium, lithium).

Second group—

Barium, strontium, calcium, magnesium.

Third group—

Aluminium, chromium (glucinum or beryllium, thorium, zirconium, yttrium, erbium, cerium, lanthanium, didymium, titanium, tantalium, niobium).

Fourth group—

Zinc, manganese, nickel, cobalt, iron (uranium, thallium, indium, vanadium).

Fifth group—

Silver, mercury, lead, bismuth, copper, cadmium (palladium, rhodium, osmium, ruthenium).

Sixth group—

Gold, platinum, tin, antimony, arsenic (iridium, molybdenum, tellurium, tungsten, selenium).

Of these metals only those printed in italics are found distributed extensively and in large quantities in that portion of the earth's crust which is accessible to our investigations; these are therefore most important to chemistry, arts and manufactures, agriculture, pharmacy, &c.; and we shall therefore dwell upon them at greater length. The remainder are more briefly considered in paragraphs printed in smaller type, which may be passed over by the younger class of students of analytical chemistry. The less important characters and reactions of the common elements, bases, and acids are also printed in smaller type. The properties and reactions of the metals themselves I have given only in the case of those that are more frequently met with in the metallic state.

§ 88.

FIRST GROUP.

More common metals:—Potassium, Sodium, Ammonium.

Rarer metals:—Cæsium, Rubidium, Lithium.

Properties of the group.—The metals of the first group—

alkali metals—are lighter than water, and decompose it, are highly oxidizable and inflammable, and have a silvery brilliant metallic lustre. The metals of the first group are generally regarded as *univalent* or *monad* elements. The hydroxides of the metals of the first group—the alkalies—are readily soluble in water, as are also the sulphides, carbonates, and phosphates of these metals. (Lithium carbonate and phosphate, however, dissolve with difficulty.) Accordingly the alkalies do not precipitate one another, nor do the alkali carbonates or phosphates (in the case of lithium, however, a high degree of dilution of the solutions is presupposed), nor are they precipitated by hydrogen sulphide under any conditions whatever. The solutions of the pure alkalies, as well as of the sulphides and carbonates of this group, restore the blue color of reddened litmus paper, and impart an intensely brown tint to turmeric paper.

Special Reactions of the more common Metals of the First Group.

§ 89.

a. POTASSIUM, K. 39.1.

1. POTASSIUM is soft as wax at common temperatures, melts at 62.5° and at a low red heat rises in green vapor. It instantly tarnishes on exposure to air, and must be kept in naphtha. Thrown on water, it burns with evolution of hydrogen, and with a purple flame, and dissolves to a bitter, caustic, alkaline solution of hydroxide, $H_2O + K = H + KOH$.

2. POTASSIUM HYDROXIDE and POTASSIUM SALTS are not volatile at a faint red heat. The hydroxide deliquesces in the air; the oily liquid formed absorbs carbon dioxide rapidly from the air, but without solidifying.

3. Nearly the whole of the POTASSIUM SALTS are soluble in water. Those with colorless acids are colorless. The normal salts with strong acids do not alter vegetable colors. Potassium carbonate crystallizes (in combination with two molecules of water) with difficulty, and deliquesces in the air. Potassium sulphate is anhydrous and suffers no alteration in the air. Use KCl for the following reactions.

4. *Hydrochloroplatinic acid* * produces in the neutral and

* *Platinic chloride* of the last edition.

acid solutions of potassium salts a yellow crystalline heavy precipitate of POTASSIUM PLATINICHLORIDE ($K_2 Pt Cl_6$). * In concentrated solutions this precipitate separates immediately upon the addition of the reagent; in dilute solutions it forms only after some time, often after a *considerable* time. Very dilute solutions are not precipitated by the reagent. The precipitate consists of octahedrons discernible under the microscope. Alkaline solutions must be acidified with hydrochloric acid before the hydrochloroplatinic acid is added. The precipitate is difficultly soluble in water; the presence of free acids does not greatly increase its solubility; it is insoluble in alcohol. Hydrochloroplatinic acid is therefore a particularly delicate test for potassium salts dissolved in alcohol. The best method of applying this reagent is to evaporate the aqueous solution of the potassium salt with hydrochloroplatinic acid nearly to dryness on the water-bath, and to pour a little water over the residue (or, better still, some alcohol), provided no substances insoluble in that menstruum be present), when the potassium platinichloride will be left undissolved. Care must be taken not to confound this salt with ammonium platinichloride, which greatly resembles it (see § 91, 5).

5. *Tartaric acid* produces, in neutral or alkaline † solutions, a white, quickly subsiding, *granular* crystalline precipitate of HYDROGEN POTASSIUM TARTRATE ($C_4 H_5 K O_6$). ‡ In concentrated solutions this precipitate separates immediately; in dilute solutions often only after the lapse of a *considerable* time. Vigorous shaking or stirring of the fluid greatly promotes its formation. Very dilute solutions are not precipitated by this reagent. Free alkalies and free mineral acids dissolve the precipitate; it is sparingly soluble in cold, but pretty readily soluble in hot water. In acid solutions the free acid must, if practicable, first be expelled by evaporation and ignition, or the solution must be neutralized with sodium hydroxide or carbonate.

Hydrogen sodium tartrate answers still better as a test for potassium than free tartaric acid. The reaction is the same in kind, but different in degree, being much more delicate with the salt than with the free acid, since where the former is used the sodium salt of the acid that was combined with the potassium is formed, whereas where free tartaric acid is the test applied, the acid originally combined with the potassium is liberated, which tends to increase the dissolving action of the water present upon the hydrogen potassium tartrate, and thus to check the separation of the latter.

* *Potassium platinic chloride* of the last edition.

† To alkaline solutions the reagent must be added until the fluid shows a strongly acid reaction.

‡ Or, $\begin{matrix} CH(OH)\text{-}COOH \\ | \\ CH(OH)\text{-}COOK. \end{matrix}$

6. If a potassic salt which is volatile at an intense red heat is held on the loop of a fine platinum wire in the fusing zone of the Bunsen *gas lamp* (p. 29), the salt volatilizes, and imparts a BLUE VIOLET tint to the part of the flame above the sample. Potassium chloride and potassium nitrate volatilize rapidly, the carbonate and sulphate less rapidly, and the phosphate still more slowly; but they all of them distinctly show the reaction, though decreasing in degree.

If it is wished to obtain a more uniform manifestation of the reaction, *i.e.*, a manifestation independent of the nature of the acid that may chance to be combined with the potassium, the sample need simply be moistened with sulphuric acid, dried at the border of the flame, and then introduced into the fusing zone. With silicates, and other potassium compounds of difficult volatility, the reaction may be insured by fusing the sample first with pure gypsum, as this serves to form calcium silicate and potassium sulphate, which latter salt then readily colors the flame. Decrepitating salts are ignited in a platinum spoon before they are attached to the loop. The sample of the potassium salt may also be held before the apex of the inner *blowpipe flame* produced with a spirit lamp. Presence of a sodium salt completely obscures the potassium coloration of the flame.

The spectrum of the potassium flame produced by the *spectroscope* (p. 37) is mapped on Plate I. It contains two characteristic lines, the red line α and the indigo blue line β. If potassium flame is observed through the *indigo prism* (p. 36) the coloration appears sky-blue, violet, and at last intensely crimson, even through the thickest layers of the solution. Admixtures of calcic, sodic, and lithic compounds do not alter this reaction, as the yellow rays cannot penetrate the indigo solution, and the rays of the lithium flame also are only able to pass through the thinner layers of that solution, but not through the thicker layers; the exact spot where the penetrating power of the rays of the lithium flame ceases has to be marked by the operator on his indigo prism. But organic substances which impart luminosity to the flame might lead to mistakes, and must therefore, if present, first be destroyed by heat. Instead of the indigo prism a blue glass may be used; if lithium is present the glass must be sufficiently thick to keep out the red lithium rays.

§ 90.

b. SODIUM, Na. 23.

1. SODIUM closely resembles potassium, melts, however, at a higher temperature, viz. 97.6°. Thrown on hot water it burns with intense yellow flame, leaving its hydroxide in solution. $H_2O + Na = Na\,O\,H + H$.

2. SODIUM HYDROXIDE and SODIUM SALTS present in general the same properties and reactions as potassium and its corresponding compounds. The oily fluid which sodium hydroxide forms by deliquescing in the air resolidifies speedily by ab-

sorption of carbon dioxide. Sodium carbonate crystallizes readily; the crystals ($Na_2CO_3 + 10H_2O$) effloresce rapidly when exposed to the air. The same applies to the crystals of sodium sulphate, $Na_2SO_4 + 10H_2O$.

3. If a sufficiently concentrated solution of a sodium salt with neutral or alkaline reaction is mixed, for greater convenience, in a watch-glass, with a solution of granular *potassium pyroantimonate* prepared according to the directions of § 54, the mixture remains clear at first, or appears only slightly turbid; but upon rubbing the part of the glass wetted by the fluid with a glass rod, a crystalline precipitate of SODIUM PYROANTIMONATE ($Sb_2O_7H_2Na_2 + 6H_2O$) speedily separates, which makes its appearance first along the lines rubbed with the rod, and subsides from the fluid as a heavy sandy precipitate. From dilute solutions of sodium salts the precipitate separates only after some time, occasionally as much as twelve hours. From very dilute solutions it does not separate at all. The precipitated sodium pyroantimonate is *invariably* crystalline. Where it has separated slowly it occasionally consists of well-formed microscopic cubic octahedrons, but more frequently of four-sided columns tapering pyramid fashion; where it has separated promptly, it appears in the form of small boat-shaped crystals. Presence of large quantities of potassium salts interferes very considerably with the reaction. Acid solutions cannot be tested with potassium pyroantimonate, as free acids will separate from the latter substance metantimonic acid. It is indispensable, therefore, before adding the reagent, to remove, if possible, the free acid by evaporation or ignition, or where this is not practicable, by neutralizing the acid solution with a little potassium carbonate until the reaction is feebly alkaline. It should also be borne in mind that only those solutions can be tested with potassium pyroantimonate which contain no other salts besides those of sodium and potassium.

4. If sodium salts are held in the fusing zone of the Bunsen *gas lamp*, or in the inner *blowpipe flame*, they show with regard to their relative volatility and the action of decomposing agents upon them, a similar deportment to the salts of potassium; the sodium salts are, however, a little less volatile than the corresponding potassium salts. But the most characteristic sign of the presence of sodium salts is the INTENSE YELLOW COLORATION which they impart to the flame. This reaction will effect the detection of even the minutest quantities of sodium, and is not obscured by the presence of large quantities of potassium salts.

The spectrum (Plate I.) shows only a single yellow line α in an ordinary *spectroscope*, but with a very powerful apparatus two lines will be visible distinctly, although they are exceedingly close to each other. The reaction is so delicate that the sodium chloride contained in atmospheric dust generally suffices to give a sodium spectrum, although a faint one.

It is characteristic of the sodium flame that a crystal of potassium dichromate appears colorless in its light, and that a slip of paper coated with mercuric iodide appears white, with a faint shade of yellow (BUNSEN); also that it looks orange yellow when observed through a *green glass* (MERZ) These reactions are not obscured by presence of salts of potassium, lithium, and calcium.

5. *Hydrochloroplatinic acid* produces no precipitate in neutral or acid solutions of sodium salts. Sodium platinichloride dissolves readily both in water and in spirit of wine; it crystallizes in long yellow prisms.

6. *Tartaric acid* and *hydrogen sodium tartrate* fail to precipitate even concentrated neutral solutions of sodium salts.

§ 91.

c. AMMONIUM, NH_4. 18.

1. AMMONIUM does not exist as such, but in the ammonium salts the group NH_4 acts as a univalent basic radical, analogous to K and Na. It probably exists in combination with mercury in the "ammonium amalgam," but if so it quickly breaks up into NH_3 and H.

2. AMMONIA (NH_3) is gaseous at the common temperature; but we have most frequently to deal with it in its aqueous solution, in which it betrays its presence at once by its penetrating odor. It is expelled from this solution by the application of heat. It may be assumed that the solution contains it as ammonium hydroxide (NH_4OH) (see § 87).

3. All the AMMONIUM SALTS are volatile at a low heat, either with or without decomposition. Most of them are readily soluble in water. The solutions are colorless. The normal compounds of ammonium with strong acids do not alter vegetable colors.

4. If AMMONIUM SALTS are triturated together with *slacked lime*, best with the addition of a few drops of water, or are, either in the solid state or in solution, heated with solution of *potassa* or of *soda*, ammonia is liberated in the gaseous state, and betrays its presence—1, by its characteristic odor; 2, by its REACTION on moistened test-papers; and 3, by giving rise to the formation of WHITE FUMES when any object (*e.g.*, a glass rod) moistened with hydrochloric acid, nitric acid, acetic acid, or any of the volatile acids, is brought in contact with it. These fumes arise from the formation of solid ammonium salts produced by the contact of the gases in the air. Hydrochloric acid is the most delicate test in this respect; acetic acid, however, admits less readily of a mistake. If the expulsion of the ammonia is effected in a small beaker, best

with slacked lime, with addition of a very little water, and the beaker is covered with a watch-glass having a slip of moistened turmeric or reddened litmus paper attached to the centre of the convex side, the reaction will show the presence of even very minute quantities of ammonia; only it is not immediate in such cases, but requires some time for its manifestation. It is promoted and accelerated by application of a gentle heat.

5. *Hydrochloroplatinic acid* shows the same deportment with ammonic salts as with salts of potassium; the yellow precipitate of AMMONIUM PLATINICHLORIDE $[(NH_4)_2 PtCl_6]$ consists, like the corresponding potassium compound, of octahedrons discernible under the microscope.

6. *Tartaric acid* throws down after some time from most highly concentrated solutions with neutral reaction, part of the ammonium as HYDROGEN AMMONIUM TARTRATE $C_4 H_5 (NH_4) O_6$. Less concentrated solutions are not precipitated. *Hydrogen sodium tartrate* precipitates concentrated solutions more completely, and produces a precipitate even in more dilute solutions. The precipitate is white and crystalline. Its separation may be promoted by shaking the glass, or rubbing it inside with a glass rod. By solvents it is acted upon like the corresponding potassium salt, only that it is a little more readily soluble in water and in acids.

§ 92.

Recapitulation and remarks.—The potassium and sodium salts are not volatile at a moderate red heat, whilst the ammonium salts volatilize readily; the latter may therefore be easily separated from the former by ignition. The expulsion of *ammonia* by slacked lime affords the surest means of ascertaining the presence of ammonium salts. Salts of potassium can be detected in the wet way only after the removal of the ammoniacal salts which may be present, since both classes of salts manifest the same or a similar deportment with hydrochloroplatinic acid and tartaric acid. After the removal of the ammonium compounds *potassium* is clearly and positively characterized by either of these two reagents. The reactions will only show in concentrated fluids; dilute solutions must therefore first be concentrated. A single drop of a *concentrated* solution will give a positive result, which cannot be obtained with a large quantity of a dilute fluid.

The most simple way of detecting potassium in the two sparingly soluble

compounds that have come under our consideration here—viz., the potassium platinichloride and the hydrogen potassium tartrate—is to decompose these salts by gentle ignition ; the former thereupon yields potassium chloride, the latter, potassium carbonate. For the direct detection of potassium in potassium iodide, tartaric acid is better suited than hydrochloroplatinic acid, since where the latter reagent is used the separation of the potassium platinichloride is interfered with in consequence of the formation of a dark red fluid containing platinum diniodide and iodide and free iodine.

Sodium is recognized (after removal of ammonium salts) by the yellow coloration which its compounds impart to the flame, even when a large proportion of potassium salts is present.

The intensity and persistence of the yellow coloration, considered in relation to the quantity of the substance which is exposed to the flame, will enable the operator, after some experience, to decide whether the sodium indicated is present in considerable quantity or only in such traces as may easily be accidental.

Potassium and sodium may both be detected readily and with great delicacy, by the flame coloration. We have seen, indeed, that the sodium coloration completely obscures the potassium coloration, even though the potassium salt contains only a trifling admixture of sodium salt. But with the aid of the spectroscope the spectra of the two are obtained so distinct and beautiful that a mistake is altogether impossible. And even without a spectroscope the potassium coloration can be distinctly recognized through the indigo prism, or through a blue glass, even in a flame colored strongly yellow by sodium, and the sodium coloration again may be placed beyond doubt, if necessary, with the aid of mercuric iodide paper, or green glass, in the manner already described.

The following methods serve for the detection of *ammonium in exceedingly minute quantities*, as, for instance, in natural waters ; they depend upon the separation of certain mercury compounds which are insoluble in water, and which contain the nitrogen or the nitrogen and part of the hydrogen of the ammonia.

a. If water containing a trace of ammonia ($\gamma\omega\nu\acute{\iota}\alpha$) or ammonium carbonate is mixed with a few drops of solution of mercuric chloride, a white precipitate is formed, even in very dilute solution; the precipitate consists of mercurammonium chloride ($N H_2Hg'' Cl$) : $2NH_3 + Hg''Cl_2 = N H_2Hg'' Cl + N H_4Cl$. If the solution is extraordinarily dilute no turbidity occurs, but on the addition of a few drops of solution of sodium carbonate, the fluid will become turbid or opalescent after a few minutes. This reaction takes place when water containing a trace of a normal ammonium salt is mixed with a few drops of solution of mercuric chloride and a few drops of solution of sodium carbonate. The precipitate which separates on the addition of sodium carbonate consists of one molecule of the previously mentioned precipitate with two molecules of mercuric oxide, $N H_3 + 2Hg'' Cl_2 + 2K_2 C O_3 = (N H_2Hg'' Cl +$

$Hg''O) + 3KCl + KHCO_3 + CO_2$. Too much mercuric chloride and sodium carbonate must not be added, otherwise a yellow precipitate of mercuric oxychloride would be formed (BOHLIG, SCHÖYEN).

b. Upon adding to a solution of potassium mercuric iodide containing potassa * a little of a fluid containing ammonia, or an ammonium salt, a reddish-brown precipitate is formed if the ammonia is present in some quantity ; but there is, at any rate, always a yellow coloration produced, even if only *most minute* traces of ammonia are present. The precipitate consists of dimercurammonium iodide ($NHg''_2I.H_2O$) ; the reaction is thus : $2(2KI, Hg''I_2) + NH_3 + 3KHO = NHg''_2I.H_2O + 7KI + 2H_2O$. Application of heat promotes the separation of the precipitate. Presence of chlorides of the alkali metals, or of salts of the alkalies with oxygen acids, does not interfere with the reaction ; but presence of potassium cyanide, and of potassium sulphide, will prevent it (J. NESSLER).

§ 93.

Special Reactions of the rarer Metals of the First Group.

1. CÆSIUM, Cs. 133, and 2. RUBIDIUM, Rb. 85.4.

The cæsium and rubidium compounds are, it would appear, found pretty widely disseminated in nature, but in very minute quantities only. They have hitherto been found chiefly in the mother liquors of mineral waters, and in a few minerals (lepidolite, melaphyr, carnallite). Cæsium has been found in considerable quantities in pollux, and traces of rubidium have been found in the ashes of plants. The cæsium and rubidium compounds bear in general great resemblance to the potassium compounds, more particularly in this, that their concentrated aqueous solutions are precipitated by *tartaric acid* and by hydrochloroplatinic acid, and also that those of them that are volatile at a red heat tinge the *flame* violet. The most notable characteristic differences, on the other hand, are that the precipitates produced by hydrochloroplatinic acid are far more insoluble in water than potassium platinichloride ; 100 grm. water will at 10° dissolve 900 mgrm. potassium platinichloride, but only 154 mgrm. of the rubidium platinichloride, and as little as 50 mgrm. of the cæsium platinichloride. Again, the alums show great differences as regards their solubility in cold water ; thus 100 parts of water at 17° dissolve 13.5 parts of potassium alum, 2.27 parts of rubidium alum, and .619 parts of cæsium alum. But above all, the flames colored by cæsium and rubidium compounds give *spectra* quite different from the potassium spectrum (see Plate I.). The cæsium spectrum is especially characterized by the two blue lines α and β, which are remarkable for their wonderful intensity and sharp outline ; also by the line γ, which, however, is less strongly marked. Among the lines in the rubidium spectrum, the splendid indigo-blue lines marked α and β strike the eye by

* Prepared as follows : Dissolve 2 grm. potassium iodide in 5 c.c. water, heat the solution, and add mercuric iodide till the last portion remains undissolved. Let the mixture cool, then dilute with 20 c.c. water. Let the fluid stand some time, filter, and mix 20 c.c. of the filtrate with 30 c.c. of a concentrated solution of potassa ; should the fluid turn turbid, filter it once more.

their extreme brilliancy. Less brilliant, but still very characteristic, are the lines δ and γ. To detect both alkalies in presence of each other by the spectroscope, the chlorides should be taken and not the carbonates, since with the latter salts the rubidium spectrum is not always distinct in the presence of the cæsium spectrum (ALLEN, HEINTZ). We have still to mention that cæsium carbonate is soluble in absolute alcohol, whilst rubidium carbonate is insoluble in that menstruum. Still, a separation of the two metals is effected only with difficulty by this means, as they seem to form a double salt which is not absolutely insoluble in alcohol. It is more easy to separate them when they are in the form of acid tartrates; the hydrogen rubidium tartrate dissolves in 8.5 parts of boiling water, and 84.57 parts of water at 25°, while the corresponding salt of cæsium dissolves in 1.02 parts of boiling water, and 10.32 parts of water at 25° (ALLEN). (The hydrogen potassium tartrate requires 15 parts of boiling water and 89 parts of water at 25°.)

[*Stannic chloride* does not affect dilute neutral solutions of cæsium chloride, but on addition of an equal volume of strong hydrochloric acid, a dense crystalline precipitate of nearly pure cæsium stannic chloride, $Sn\,Cs_2\,Cl_6$, is thrown down which is but slightly soluble in hydrochloric acid (SHARPLESS). Ammonium salts give a similar reaction, and must be removed by ignition. To purify the cæsium precipitate, wash it with strong HCl, dissolve in boiling water containing some HCl, and throw down again with strong HCl (STOLBE). —ED.]

3. LITHIUM, Li. 7.

Lithium is also found pretty widely disseminated in nature, but in minute quantities only. It is often met with in the analysis of mineral waters and ashes of plants, less frequently in the analysis of minerals, and only rarely in that of technical and pharmaceutical products. Lithium forms the transition from the first to the second group. Its hydroxide dissolves with difficulty in water; it does not attract moisture from the air. Most of its salts are soluble in water; some of them are deliquescent (lithium chloride). Lithium carbonate is difficultly soluble, particularly in cold water. *Hydrogen sodium phosphate* produces in not over-dilute solutions of salts of lithium upon boiling, a white crystalline precipitate of lithium phosphate ($Li_3\,PO_4 + \frac{1}{2}H_2O$) which quickly subsides to the bottom of the precipitating vessel. This reaction, which is characteristic of lithium, is rendered much more delicate by adding with the sodium phosphate a little solution of soda, just sufficient to leave the reaction alkaline, evaporating the mixture to dryness, treating the residue with water, and adding an equal volume of liquid ammonia. By this course of proceeding even very minute quantities of lithium will be separated as $Li_3\,PO_4 + \frac{1}{2}H_2O$. The precipitate fuses before the blowpipe, and gives upon fusion with sodium carbonate a clear bead; when fused upon charcoal it is absorbed by the pores of the latter body. It dissolves in hydrochloric acid to a fluid which, when diluted and supersaturated with ammonia, remains clear in the cold, but upon boiling gives a heavy crystalline precipitate of $Li_3\,PO_4 + \frac{1}{2}H_2O$. (Reactions by which the lithium phosphate differs from the phosphates of the alkali-earth metals.) *Tartaric acid* and *hydrochloroplatinic acid* fail to precipitate even concentrated solutions of lithic salts. If salts of lithium are exposed to the *gas* or *blowpipe flame*, in the manner described § 89, 5, they tinge the flames carmine-red. Silicates containing lithium re-

quire addition of gypsum to produce this reaction. Lithium phosphate will tinge the flame carmine-red if the fused bead is moistened with hydrochloric acid. The sodium coloration conceals the lithium coloration; in presence of sodium, therefore, the lithium tint must be viewed through a blue glass, or through a thin layer of indigo solution. Presence of a small proportion of potassium will not conceal the lithium coloration. In presence of a large proportion of potassium, the lithium may be identified by placing the substance in the fusing zone, viewing the colored flame through the indigo prism and comparing it with a pure potassium flame produced in the opposite part of the fusing zone. Viewed through thin layers, the lithium colored flame appears now redder than the pure potassium flame; viewed through somewhat thicker layers, the flames appear at last equally red, if the proportion of the lithium to the potassium is only trifling; but when lithium predominates in the examined sample the intensity of the red coloration imparted by lithium decreases perceptibly when viewed through thicker layers, whilst the pure potassium flame is scarcely impaired thereby. By this means lithium may be detected in potassium salts, even though present only in the proportion of one part in several thousand parts of the latter. Sodium, unless present in overlarge quantities, interferes but little with these reactions (CARTMELL, BUNSEN).

The *lithium spectrum* (Plate I.) is most brilliantly characterized by the splendid carmine-red line α, and the orange-yellow very faint line β. The flame of a Bunsen burner yields only these two lines, but if lithium chloride is introduced into a hydrogen flame, a dull blue line is perceptible which becomes brilliant if the oxyhydrogen flame is used. Its position almost coincides with the weaker of the two blue lines of cæsium (TYNDALL, FRANKLAND). If alcohol be poured over lithium chloride, and then ignited, the flame shows also a carmine-red tint. Presence of sodium salts will mask this reaction.

To detect small quantities of cæsium, rubidium, and lithium in presence of very large quantities of sodium or potassium, extract the dry chlorides, with addition of a few drops of hydrochloric acid, with alcohol of 90 per cent., which leaves behind the far larger portion of the sodium chloride and potassium chloride. Evaporate the solution to dryness, dissolve the residue in a little water, and precipitate with hydrochloroplatinic acid. Filter the fluid off, boil the precipitate repeatedly with small quantities of water, to remove the potassium platinichloride present, and examine in the course of this process repeatedly by the spectroscope. The potassium spectrum will now be found to grow fainter and fainter, whilst the spectra of rubidium and cæsium will become visible, if these metals are present. Evaporate the fluid filtered off from the platinum, precipitate to dryness, heat the residue to slight redness in a current of hydrogen, to decompose the sodium platinichloride and the excess of hydrochloroplatinic acid, moisten with hydrochloric acid, drive off the acid again, and extract the lithium chloride finally with a mixture of absolute alcohol and ether. The evaporation of the solution obtained leaves the lithium chloride behind in a state of almost perfect purity; it may then be further examined and tested. Before drawing from the simple coloration of the flame the conclusion that lithium is present, it is advisable, in order to guard against the chance of error, to test a portion of the residue, dissolved in water, with sulphuric acid and alcohol, to make quite sure that strontium or calcium is not present. The addition of hydrochloric acid, which is repeat-

edly prescribed in the above process to precede the extraction of the lithium chloride with alcohol, is necessary for this reason, that lithium chloride is, even at a moderate red heat, converted by the action of aqueous vapor into lithium hydroxide, which then attracts carbonic acid, forming lithium carbonate, which is insoluble in alcohol.

§ 94.

SECOND GROUP.

Barium, Strontium, Calcium, Magnesium.

Properties of the group.—The alkali-earth metals have a brilliant lustre. Their color is white (barium and magnesium) or yellow (strontium and calcium). They are heavier than water and decompose water (magnesium slowly) at common temperatures. They are regarded as bivalent or dyad elements. The monoxides and corresponding hydroxides of the metals of the second group are termed the alkali-earths, the monoxides when put in contact with water unite with it to form hydroxides, which dissolve in additional water. Magnesium oxide and hydroxide, however, dissolve but very sparingly in water. The solutions manifest alkaline reaction; the alkaline reaction of magnesia is most clearly apparent when that earth is laid upon moistened test-paper. The neutral carbonates and phosphates of the alkali-earth metals are insoluble in water; the solutions of their salts are therefore precipitated by carbonates and phosphates of the alkali metals. This reaction distinguishes the metals of the second group from those of the first. From the metals of the other groups they are distinguished by the solutions being neither precipitated by hydrogen sulphide, nor by ammonium sulphide. The alkali earths and the salts of their metals are white or colorless, and not volatile at a moderate red heat. The solutions of the nitrates and chlorides of this group are not precipitated by barium carbonate.

Special Reactions.

§ 95.

a. Barium, Ba. 137.

1. Barium hydroxide, $Ba(OH)_2$, is pretty readily soluble in hot water, but rather sparingly so in cold water; it dissolves freely in dilute hydrochloric or nitric acid. It fuses at a red heat without losing water.

2. Most of the BARIUM SALTS are insoluble in water. The soluble salts do not affect vegetable colors, and are decomposed upon ignition in a glass tube, with the exception of chloride, bromide, and iodide of barium. The insoluble salts dissolve in dilute hydrochloric acid, except barium sulphate and barium silico-fluoride.

BARIUM CHLORIDE and NITRATE are insoluble in alcohol, and do not deliquesce in the air. Concentrated solutions of barium salts are precipitated by hydrochloric or nitric acid added in large proportions, as barium chloride and nitrate are not soluble in the aqueous solutions of the said acids.

3. *Ammonia* produces no precipitate in aqueous solutions of barium salts.

Potassa or *soda* (free from carbonic acid) precipitate only from highly concentrated solutions crystals of BARIUM HYDROXIDE ($Ba H_2O_2 + 8$ aq.) which redissolve in water.

4. *Soluble carbonates* (*of the alkali metals*) throw down BARIUM CARBONATE ($Ba C O_3$) in the form of a white precipitate. If the solution was previously acid, complete precipitation takes place only upon heating the fluid. In ammonium chloride the precipitate is soluble to a trifling yet clearly perceptible extent; ammonium carbonate therefore produces no precipitate in very dilute baric solutions containing much ammonium chloride.

5. *Sulphuric acid* and all the soluble *sulphates*, more particularly also solution of *calcium sulphate*, produce, even in very dilute solutions, a heavy, finely pulverulent, white precipitate of BARIUM SULPHATE ($Ba S O_4$), which is insoluble in alkalies, nearly so in dilute acids, but perceptibly soluble in boiling concentrated hydrochloric and nitric acids, as well as in concentrated solutions of ammonium salts; however, in these latter only if there is no excess of sulphuric acid or a sulphate present. This precipitate is generally formed immediately upon the addition of the reagent; from highly dilute solutions, however, especially when strongly acid, it separates only after some time.

6. *Hydrofluosilicic acid* throws down BARIUM SILICO-FLUORIDE ($Ba F_2 . Si F_4$) in the form of a colorless crystalline quickly subsiding precipitate. In dilute solutions this precipitate is formed only after the lapse of some time; it is perceptibly soluble in hydrochloric and nitric acids. Addition of an

equal volume of alcohol hastens the precipitation and makes it so complete that the filtrate remains clear upon addition of sulphuric acid.

7. *Sodium phosphate* produces in neutral or alkaline solutions a white precipitate of BARIUM HYDROGEN PHOSPHATE ($BaHPO_4$), which is soluble in free acids.

Addition of ammonia only slightly increases the quantity of this precipitate, a portion of which is in this process converted into barium phosphate, $Ba_3(PO_4)_2$. Ammonium chloride dissolves the precipitate to a clearly perceptible extent.

8. *Ammonium oxalate* produces in moderately dilute solutions a white pulverulent precipitate of BARIUM OXALATE ($C_2O_4Ba \cdot H_2O$), which is soluble in hydrochloric and nitric acids.

When recently thrown down, this precipitate dissolves also in oxalic and acetic acids; but the solutions speedily deposit barium binoxalate [$(C_2O_4H)_2Ba \cdot 4H_2O$] in the form of a crystalline powder.

9. *Potassium chromate* and dichromate produce a bright yellow precipitate of barium chromate ($BaCrO_4$) even in very dilute solutions of baric salts. The precipitate dissolves readily in hydrochloric or nitric acid to a yellowish-red solution, from which it is thrown down again by ammonia.

acetic acid

10. If baric salts are held on the loop of a platinum wire in the fusing zone of the Bunsen *gas flame*, the part of the flame above the sample is colored YELLOWISH GREEN; or if the baric salts are held in the inner *blowpipe flame*, the same coloration is imparted to the part of the flame beyond the sample. With the soluble baric salts, and also with the barium carbonate and sulphate, the reaction is immediate or very soon, but the phosphate requires previous moistening of the sample with sulphuric acid or hydrochloric acid, by which means the barium may be detected by the flame coloration also in silicates decomposable by acids. Silicates which hydrochloric acid fails to decompose must be fused with sodium carbonate, when the barium carbonate produced will show the reaction. It is characteristic of the yellowish-green barium coloration of the flame that it appears bluish-green when viewed through the green glass. If the sulphates are selected for the experiment, presence of calcium and strontium will not interfere with the reaction. The barium *spectrum* is shown in Plate I. The green lines α and β are the most in-

tense; γ is less marked, but still characteristic. The platinum wire sometimes contains barium (KRAUT), hence it is well to see first whether it will give a barium spectrum by itself.

11. Barium sulphate is readily decomposed by fusion with sodium carbonate, which results in the formation of sodium sulphate, soluble in water, and of barium carbonate, insoluble in that menstruum.

Cold solutions of *hydrogen carbonates of the alkali metals* or of *ammonium carbonate*, fail to decompose barium sulphate, or to speak more correctly, they decompose that salt only to a scarcely perceptible extent; the same applies to a boiling solution of 1 *part of potassium carbonate and* 3 *parts of potassium sulphate*. Repeated action of boiling solution of sodium or potassium carbonate upon barium sulphate succeeds in the end completely in decomposing that salt.

§ 96.

b. STRONTIUM, Sr. 87.6.

1. STRONTIUM HYDROXIDE and the STRONTIUM SALTS have nearly the same general properties and reactions as the corresponding barium compounds. Strontium hydroxide is more sparingly soluble in water than barium hydroxide.

STRONTIUM CHLORIDE dissolves in absolute alcohol and deliquesces in moist air. Strontium nitrate is insoluble in absolute alcohol and does not deliquesce in the air.

2. The salts of strontium show with *ammonia*, *potassa*, and *soda*, and also with the *carbonates of the alkali metals*, and with *sodium phosphate*, nearly the same reactions as the barium salts. Strontium carbonate dissolves somewhat more difficultly in ammonium chloride than barium carbonate.

3. *Sulphuric acid and sulphates* throw down STRONTIUM SULPHATE ($Sr\,S\,O_4$) in the form of a white precipitate. Thrown down by dilute sulphuric acid from concentrated solutions, it is at first flocculent and amorphous, afterwards pulverulent and crystalline; thrown down by dilute sulphuric acid from dilute solutions, or produced by solutions of sulphates, it is immediately pulverulent and crystalline. Application of heat promotes the precipitation. Strontium sulphate is less insoluble in water than barium sulphate; hence it separates from rather dilute solutions only after some time; and this is invariably the case (even in concentrated solutions) if solution of *calcium sulphate* is used as precipitant. In hydrochloric acid and in nitric acid, strontium sulphate dissolves

perceptibly. Presence of large quantities of these acids will accordingly most seriously impair the delicacy of the reaction.

4. *Hydrofluosilicic acid* fails to produce a precipitate even in concentrated solutions; even upon addition of an equal volume of alcohol no precipitation takes place, except in very highly concentrated solutions.

5. *Ammonium oxalate* precipitates even from rather dilute solutions STRONTIUM OXALATE, in the form of a white powder, which dissolves readily in hydrochloric and nitric acid, and perceptibly in ammonium salts, but is only sparingly soluble in oxalic and acetic acid.

6. *Potassium dichromate* does not precipitate solutions of salts of strontium, even when they are concentrated. *Potassium chromate* at first produces no precipitate, but on long standing, if the solution is not very dilute, light yellow strontium chromate separates in the crystalline form. The crystals are but slightly soluble in water, but readily soluble in hydrochloric, nitric, and chromic acids.

7. If a strontium salt is held in the fusing zone of the Bunsen *gas flame*, or in the inner *blowpipe flame*, an INTENSELY RED COLOR is imparted to the flame.

The reaction is the most distinct with strontium chloride, less clear with hydroxide and carbonate, fainter still with sulphate, and scarcely appears with strontium salts of fixed acids. The sample, is therefore, after its first exposure to the flame, moistened with hydrochloric acid, and then again exposed to the flame. If strontium sulphate is likely to be present, the sample is first exposed a short time to the reducing flame (to produce strontium sulphide), before it is moistened with hydrochloric acid. Viewed through the *blue glass*, the strontium flame appears purple or rose (difference between strontium and calcium, which latter body shows a faint greenish-gray color when treated in this manner); this reaction is the most clearly apparent if the sample is moistened with hydrochloric acid when brought into the flame. In presence of barium, the strontium reaction shows only upon the first introduction of the sample moistened with hydrochloric acid into the flame. The strontium *spectrum* is shown in Plate I. It contains a number of characteristic lines, more especially the orange line α, the red lines β and γ, and the blue line δ, which latter is more particularly suited for the detection of strontium, in presence of barium and calcium.

8. Strontium sulphate is completely decomposed by boiling with solution of sodium carbonate.

It is also decomposed by digestion with solutions of *ammonium carbonate* or of *hydrogen alkali carbonates*, but much more rapidly by boiling with a solution of 1 part of *potassium carbonate and* 3 *parts of potassium sulphate* (essential difference between strontium sulphate and barium sulphate).

§ 97.

c. Calcium, Ca. 40.

1. Calcium oxide (quicklime), calcium hydroxide (slacked lime) and calcium salts present in their general properties and reactions, a great similarity to the corresponding barium and strontium compounds. Calcium hydroxide is far more difficultly soluble in water than the barium and strontium hydroxides; it dissolves also more sparingly in hot than in cold water. Calcium hydroxide loses its water upon ignition.

Calcium chloride and nitrate are soluble in absolute alcohol and deliquesce in the air.

2. *Ammonia, potassa, carbonates of the alkali metals* and *sodium phosphate* show nearly the same reactions with calcium as with barium salts.

Recently precipitated calcium carbonate ($Ca\,C\,O_3$) is bulky and amorphous —after a time, and immediately upon application of heat, it shrinks and assumes a crystalline form. Recently precipitated calcium carbonate dissolves pretty readily in solution of ammonium chloride; but the solution speedily becomes turbid, and deposits the greater part of the dissolved salt in form of crystals.

3. *Sulphuric acid* and *sodium sulphate* produce immediately in highly concentrated solutions, white precipitates of calcium sulphate ($Ca\,S\,O_4 . 2H_2O$), which redissolve completely in a large proportion of water, and are far more soluble in acids. In less concentrated solutions the precipitates are formed only after the lapse of some time; and no precipitation whatever takes place in dilute solutions. Solutions of calcium sulphate, of course, cannot produce a precipitate in calcium salts; but even a cold saturated solution of potassium sulphate, mixed with 3 parts of water, produces a precipitate only after standing from twelve to twenty-four hours. In solutions of calcium salts which are so very dilute that sulphuric acid has no apparent action on them, a precipitate will form upon addition of two volumes of alcohol either immediately, or after the lapse of some time.

4. *Hydrofluosilicic acid* does not precipitate calcium salts, even when an equal volume of alcohol is added.

5. *Ammonium oxalate* produces a white pulverulent precipitate of calcium oxalate. If the fluids are in any degree concentrated or hot, the precipitate ($C_2\,Ca\,O_4 . 2$ aq.) forms at once; but if they are very dilute and cold, it forms only after

some time, in which latter case it is more distinctly crystalline and consists of a mixture of the above salt with $C_2 Ca O_4 . 6$ aq. Calcium oxalate dissolves readily in hydrochloric and nitric acids; but acetic and oxalic acids fail to dissolve it to any perceptible extent.

6. Neither *potassium chromate* nor *dichromate* precipitate solutions of salts of calcium.

7. If calcium salts are held in the fusing zone of the Bunsen *gas flame*, or in the inner *blowpipe flame*, they impart to the flame a YELLOWISH-RED color.

This reaction is the most distinct with calcium chloride; calcium sulphate shows it only after its incipient decomposition, and calcium carbonate also most distinctly after the escape of the carbonic acid. Compounds of calcium with fixed acids do not color flame; those of them which are decomposed by hydrochloric acid will, however, show the reaction after moistening with that acid. The reaction is in such cases promoted by flattening the loop of the platinum wire, placing a small portion of the calcic compound upon it, letting it frit, adding a drop of hydrochloric acid, which remains hanging to the loop, and then holding the latter in the fusing zone. Viewed through the *green glass* the calcium coloration of the flame appears finch-green colored on bringing the sample moistened with hydrochloric acid into the flame (difference between calcium and strontium, which latter substance under similar circumstances shows a very faint yellow (MERZ). In presence of barium the calcium reaction shows only upon the first introduction of the sample into the flame. The *calcium spectrum* is shown in Plate I. The intensely green line β is more particularly characteristic, also the intensely orange line α. It requires a very good apparatus to show the indigo-blue line to the right of G in the solar spectrum, as this is much less luminous than the other lines.

8. With carbonates and hydrogen carbonates of the alkali metals, also with a solution of potassium carbonate and sulphate, calcium sulphate shows the same reactions as strontium sulphate.

§ 98.

d. MAGNESIUM, Mg. 24.

1. MAGNESIUM is silver white, hard, ductile, of 1.74 sp. gr. It melts at a moderate red heat, and volatilizes at a white heat. When ignited in the air it burns with a dazzling white flame to magnesium oxide. It preserves its lustre in dry air, but it gradually becomes coated with hydroxide when exposed to moist air. Pure water is not decomposed by magnesium at the ordinary temperature, but in water acidulated with hydrochloric or sulphuric acid, magnesium dissolves rapidly with evolution of hydrogen.

2. MAGNESIUM OXIDE and HYDROXIDE are white powders of far greater bulk

than the other oxides and hydroxides of this group, and are nearly insoluble both in cold and hot water. The hydroxide loses water upon ignition.

3. Some of the SALTS OF MAGNESIUM are soluble in water, others are insoluble in that fluid. The soluble salts have a nauseous bitter taste; the normal salts do not alter vegetable colors; with the exception of the sulphate, they undergo decomposition when gently ignited, and the greater part of them even upon simple evaporation of their solutions. Magnesium sulphate loses its acid at a white heat. Nearly all the magnesium salts which are insoluble in water dissolve readily in hydrochloric acid.

4. *Ammonia* throws down from the solutions of normal salts part of the magnesium as HYDROXIDE ($Mg(OH)_2$) in the form of a white bulky precipitate. The rest of the magnesium remains in solution as a double salt, viz., in combination with the ammonium salt which forms upon the decomposition of the magnesium salts.

These double salts are not decomposed by a small excess of ammonia. It is owing to this tendency of magnesium salts to form such double salts with ammonic compounds that ammonia fails to precipitate them in presence of a sufficient proportion of an ammonium salt with neutral reaction; or, what comes to the same, that ammonia produces no precipitate in solutions of magnesium containing a sufficient quantity of free acid, and that precipitates produced by ammonia in neutral solutions of magnesium are redissolved upon the addition of ammonium chloride. It should be borne in mind that in solutions containing only 1 molecule of an ammonium salt [$(NH_4)_2SO_4$ or NH_4Cl] to 1 molecule of magnesium salt, although no precipitate is produced by the addition of a slight excess of ammonia, a portion of the magnesium is, however, thrown down on the addition of a large excess of ammonia.

5. *Potassa, soda, baryta* and *lime* throw down MAGNESIUM HYDROXIDE. The separation of this precipitate is greatly promoted by boiling the mixture. Ammonium chloride and other similar ammonium salts redissolve the washed precipitated hydroxide. If the ammonium salts are added in sufficient quantity to the magnesium solution before the addition of the precipitant, small quantities of the latter fail altogether to produce a precipitate.

However, upon boiling the solution afterwards with an excess of potassa, the precipitate will of course make its appearance, since this process causes the decomposition of the ammonium salt, removing thus the agent which retains the magnesium hydroxide in solution. It should be remembered that magnesium hydroxide is more soluble in solutions of potassium chloride, sodium chloride, potassium sulphate, and sodium sulphate than in water, and that on this account its precipitation is less complete when these salts are present in large quantities. From such solutions the magnesium is, however, thrown down, for the most part, by an excess of solution of potassa or solution of soda.

6. *Potassium carbonate* and *sodium carbonate* produce in neutral solutions a white precipitate of BASIC MAGNESIUM CARBONATE, $4\,Mg\,(O\,H)_2 . 4\,Mg\,C\,O_3 + 10\,aq.$ One-fifth of the carbonic acid of the decomposed alkali carbonate is liberated in the process, and combines with a portion of the magnesium carbonate to bicarbonate, which remains in solution. This acid carbonate is decomposed by boiling, and an additional precipitate formed ($Mg\,CO_3 + 3$ aq.) while carbon dioxide escapes. Application of heat therefore promotes the separation and increases the quantity of the precipitate. Ammonium chloride and other similar ammonium salts, when present in sufficient quantity, prevent this precipitation also, and readily redissolve the precipitates after they have been washed.

7. If magnesium solutions are mixed with *ammonium carbonate*, the fluid always remains clear at first; but after standing some time, it deposits more or less quickly, according to the concentration of the solution, a crystalline precipitate. When the ammonium carbonate is in slight excess, the precipitate consists of magnesium carbonate ($Mg\,C\,O_3 + 3$ aq.), when the ammonium carbonate is in large excess, it consists of MAGNESIUM AMMONIUM CARBONATE ($Mg\,(N\,H_4)_2\,(C\,O_3)_2 + 4$ aq.). In highly dilute solutions this precipitate will not form. Addition of ammonia and of excess of ammonium carbonate promotes its separation. Ammonium chloride prevents the formation of the precipitate, except in concentrated solutions.

8. *Sodium phosphate* precipitates from magnesium solutions, if they are not too dilute, MAGNESIUM HYDROGEN PHOSPHATE ($Mg\,H\,P\,O_4 + 7$ aq.) as a white powder. Upon boiling, magnesium phosphate ($Mg_3(P\,O_4)_2 + 7$ aq.) separates, even from rather dilute solutions. But if the addition of the precipitant is preceded by that of *ammonium chloride* and *ammonia* a white crystalline precipitate of AMMONIUM MAGNESIUM PHOSPHATE ($N\,H_4\,Mg\,P\,O_4 + 6$ aq.) will separate even from very dilute solutions of magnesium; its separation may be greatly promoted and accelerated by stirring with a glass rod; even should the solution be so extremely dilute as to forbid the formation of a precipitate, yet the lines of direction in which the glass rod has moved along the inside of the vessel will after the lapse of some time appear distinctly as white streaks (soluble in hydrochloric acid). Water and solutions of ammonium salts dissolve the precipitate but very slightly; but it is readily soluble in acids, even in acetic acid. In water containing ammonia it may be considered insoluble.

9. *Ammonium oxalate* produces no precipitate in highly dilute solutions of magnesium; in less dilute solutions no precipitate is formed at first, but after standing some time crystalline crusts of various double oxalates of ammonium and magnesium make their appearance. In highly concentrated solutions ammonium oxalate very speedily produces precipitates of magnesium oxalate ($Mg\ C_2O_4.2\ aq.$), which contain small quantities of the above-named double salts. Ammonium chloride, especially in presence of free ammonia, interferes with the formation of these precipitates, but will not in general absolutely prevent it.

10. *Sulphuric acid*, *hydrofluosilicic acid*, and *potassium chromate* do not precipitate salts of magnesium.

11. Salts of magnesium do not color flame.

§ 99.

Recapitulation and remarks.—The difficult solubility of the magnesium hydroxide, the ready solubility of the sulphate (unless it is present in the natural form, either anhydrous or combined with 1 molecule of water), and the disposition of magnesium salts to form double salts with ammonium compounds, are the three principal points in which magnesium differs from the other alkali-earth metals. To detect magnesium in solutions containing all the alkali-earth metals, we always first remove the barium, strontium, and calcium. This is effected most conveniently by means of ammonium carbonate, with addition of some ammonia and of ammonium chloride, and application of heat; since by this process the barium, strontium, and calcium are obtained in a form of combination suited for further examination. If the solutions are somewhat dilute, and the precipitated fluid is quickly filtered, the carbonates of barium, strontium, and calcium are obtained on the filter, whilst the whole of the magnesium is found in the filtrate. But as ammonium chloride dissolves a little barium carbonate, and also a little calcium carbonate, though much less of the latter than of the former, trifling quantities of these bases are found in the filtrate; nay, where only traces of them are present, they may altogether remain in solution.

In accurate experiments, therefore, the separation is effected in the following way: Divide the filtrate into three

portions, test one portion with dilute sulphuric acid for the trace of barium which it may contain in solution, and another portion with ammonium oxalate for the minute trace of calcium which may have remained in solution. If the two reagents produce no turbidity even after some time, test the third portion with sodium phosphate for MAGNESIUM. But if one of the reagents causes turbidity, filter the fluid from the gradually subsiding precipitate, and test the filtrate for magnesium. Should both reagents produce precipitates, mix the first two portions together, filter after some time, and then test the filtrate. To make sure that the precipitate thrown down by ammonium oxalate is actually calcium oxalate, and not, as it may be, oxalate of magnesium and ammonium, dissolve it in very little hydrochloric acid, and add dilute sulphuric acid, and then alcohol.

To show the presence of barium, strontium, and calcium in the precipitate produced by ammonium carbonate, dissolve the precipitate in some dilute hydrochloric acid; add solution of gypsum to a small portion of this solution, when the immediate formation of a precipitate will prove the presence of BARIUM. Evaporate the remainder of the hydrochloric acid solution on the water-bath to dryness, and treat the residue with absolute alcohol, which will dissolve the strontium chloride and the calcium chloride, leaving the greater part of the barium chloride undissolved. Mix the alcoholic solution with an equal volume of water and a few drops of hydrofluosilicic acid, and let the mixture stand several hours, when the last traces of the barium present will be found precipitated as barium silicofluoride. Filter, and add sulphuric acid to the alcoholic filtrate. This will throw down the strontium and the calcium. Filter the fluid from the precipitate, wash with weak alcohol, and boil the sulphates for some time with a sufficient quantity of sodium carbonate, wash thoroughly, dissolve in hydrochloric acid, remove excess of acid by evaporation, dissolve the residual chlorides in water, test a small portion of the solution for STRONTIUM with calcium sulphate. If strontium is present precipitate it from the reserved portion of the solution by the addition of potassium sulphate and test the filtrate for CALCIUM with ammonium oxalate.

Or dissolve the strontium and calcium carbonates in nitric acid, evaporate the solution to dryness, pulverize the residue and digest it for a considerable

time with absolute alcohol to which a little ether has been added, when the calcium nitrate will dissolve, leaving the strontium nitrate undissolved. The latter may be readily examined, by dissolving in a small quantity of water and adding solution of calcium sulphate ; the calcium in the alcoholic solution of calcium nitrate may be detected by the addition of sulphuric acid. The precipitate of calcium sulphate thus produced, when treated with water, should yield a solution which gives an immediate and considerable precipitate with ammonium oxalate.

The best and most convenient way of detecting the alkali-earth metals in their *phosphates*, is to decompose these latter by means of ferric chloride with addition of sodium acetate (§ 142). The *oxalates* of this group are converted into carbonates by ignition, preparatory to the detection of the several metals which they may contain.

The following method will serve to analyze mixtures of the *sulphates* of the alkali-earth metals : Extract the mixture under examination with small portions of boiling water. The solution contains the whole of the magnesium sulphate unless it is present in the native anhydrous state, besides a trifling quantity of calcium sulphate. Digest the residue, according to H. ROSE's direction, in the cold for 12 hours, with a solution of ammonium carbonate, or boil it 10 minutes with a solution of 1 part of carbonate and 3 parts of sulphate of potassium, filter, wash, then treat with dilute hydrochloric acid, which will dissolve the carbonates of strontium and calcium formed, and if the anhydrous native magnesium sulphate was present, the magnesium carbonate or the ammonium magnesium carbonate, but always also a minute trace of barium (FRESENIUS), leaving behind the undecomposed barium sulphate. The latter may then be decomposed by fusion with alkali carbonates. The solutions obtained are to be examined further according to the above directions.

The detection of barium, strontium and calcium in the moist way is very instructive, but also very laborious and tedious. By means of the spectroscope these metals are much more readily detected even when present all three together. According to the nature of the acid, the sample is either introduced into the flame directly, or after previous ignition or moistening with hydrochloric acid. To detect very minute quantities of barium and strontium in presence of large quantities of calcium, ignite a few grammes of the mixed carbonates a few minutes in a platinum crucible strongly over the blast,* extract the ignited mass by boiling with a little distilled water, evaporate with hydrochloric acid to dryness, and examine the residue by spectrum analysis (ENGELBACH).

§ 100.

THIRD GROUP.

More common metals :—ALUMINIUM, CHROMIUM.

Rarer metals :—GLUCINUM, THORIUM, ZIRCONIUM, YTTRIUM, ERBIUM, CERIUM, LANTHANIUM, DIDYMIUM, TITANIUM, TANTALIUM, NIOBIUM.

Properties of the group.—The oxides and hydroxides of the third group are insoluble in water. Their sulphides cannot

* The carbonates of barium and strontium are much more readily reduced to the caustic state in this process than would be the case in the absence of calcium carbonate.

be produced in the moist way. Hydrogen sulphide, therefore, fails to precipitate the solutions of their salts. Ammonium sulphide throws down from the solutions of the salts in which the metals of the third group constitute the base,* the hydroxides in the same way as ammonia. The reaction with ammonium sulphide distinguishes the metals of the third from those of the two preceding groups.

Special Reactions of the more common Metals of the Third Group.

§ 101.

a. ALUMINIUM, Al. 27.4.†

1. ALUMINIUM is nearly white. It is not oxidized by the action of the air, in compact masses not even upon ignition. It may be filed, and is very malleable; its specific gravity is only 2.67. It is fusible at a bright red heat. It does not decompose water at a boiling heat. Aluminium dissolves readily in hydrochloric acid, as well as in hot solution of potassa, with evolution of hydrogen. Nitric acid dissolves it only slowly, even with the aid of heat.

2. ALUMINIUM OXIDE (Al_2O_3) or ALUMINA is non-volatile and colorless; the HYDROXIDES are also colorless. Alumina dissolves in dilute acids slowly and with very great difficulty, but more readily in concentrated hot hydrochloric acid. In fusing sodium disulphate, it dissolves readily to a mass soluble in water. The trihydroxide in the amorphous condition is readily soluble in acids; in the crystalline state it dissolves in them with very great difficulty. By ignition with alkalies, an aluminate is formed which readily dissolves in acids.

3. The ALUMINIUM SALTS are colorless and non-volatile; some of them are soluble, others insoluble. The anhydrous chloride is solid, pale yellow, crystalline, volatile. The soluble salts have a sweetish, astringent taste, redden litmus paper, and lose their acid upon ignition. The insoluble salts are dissolved by hydrochloric acid, with the exception of certain native compounds; the aluminium compounds which are insoluble in hydrochloric acid are made soluble by ignition with sodium carbonate, or sodium disulphate. Their decomposition and solution may be effected also by heating them, reduced to a fine powder, with hydrochloric acid of 25 per cent., or with a mixture of 3 parts by weight of sulphuric acid, and 1 part by weight of water, in sealed glass tubes, to 200°–210° for two hours (A. MITSCHERLICH).

* While the metals of the third group act as bases towards strong acids, they also deport themselves as acids towards strong bases. Aluminium, its oxide and its hydroxide, dissolve in sulphuric acid to form aluminium sulphate $Al_2(SO_4)_3$ and in potassa, yielding potassium aluminate $Al_2(KO)_6$, or $Al(KO)_3$.

† Aluminium in all its known compounds is apparently a triad. It is, however, probable that two tetrad atoms of this element are usually associated as a sexivalent group, e.g.:—

$$Al_2O_3 = \begin{matrix} Al{=}O \\ | \\ Al{=}O \end{matrix} > O \quad \text{and} \quad Al_2Cl_6 = \begin{matrix} Al\langle Cl \\ | \\ Al\langle Cl \end{matrix}\begin{matrix} Cl \\ Cl \\ Cl \\ Cl \end{matrix}$$

4. *Potassa* and *soda* throw down from solutions of aluminium salts a bulky precipitate of ALUMINIUM HYDROXIDE, $Al_2(OH)_6$, which contains alkali and generally also an admixture of basic salt; this precipitate redissolves readily and completely in an excess of the precipitant, but from this solution $Al_4(OH)_6$ is reprecipitated by addition of ammonium chloride, even in the cold, but more completely upon application of heat (compare § 56). The precipitate does not dissolve in excess of ammonium chloride.

5. *Ammonia* also produces a precipitate of ALUMINIUM HYDROXIDE, which contains ammonia and an admixture of basic salt; this precipitate redissolves to a very slight extent in a large excess of the precipitant. This solubility is lessened by ammonium salts.

Boiling promotes precipitation, as it drives off the excess of ammonia. It is this deportment which accounts for the complete precipitation of aluminium hydroxide from solution in potassa by an excess of ammonium chloride.

6. *Sodium carbonate* precipitates BASIC ALUMINIUM CARBONATE, which is somewhat soluble in excess of fixed alkali carbonate, and still less soluble in excess of ammonium carbonate. Boiling promotes precipitation by the latter.

7. If the solution of an aluminium salt is digested with finely divided *barium carbonate*, the greater part of the acid of the aluminium salt combines with the barium, the liberated carbonic acid escapes, and the aluminium precipitates completely as HYDROXIDE MIXED WITH BASIC SALT; even digestion in the cold suffices to produce this reaction.

N.B. to 4, 5, 6 and 7.—Tartaric, citric, and other non-volatile organic acids completely prevent the precipitation of aluminium as hydroxide or basic salt, when they are present in any notable quantity. The presence of sugar and similar organic substances interferes with the completeness of the precipitation.

8. *Sodium phosphate* precipitates ALUMINIUM PHOSPHATE ($Al PO_4$) from solutions of aluminium salts. The bulky white precipitate is readily soluble in potassa or soda solution, but not in ammonia; ammonium chloride therefore precipitates it from its solution in potassa or soda. The precipitate is readily soluble in hydrochloric or nitric acid, but not in acetic acid (difference from aluminium hydroxide); sodium acetate, therefore, precipitates it from its solution in hydrochloric acid, if the latter is not too predominant. Tartaric acid, sugar, etc., do not prevent the precipitation of aluminium phosphate, but citric acid does prevent it (GROTHE).

9. *Oxalic acid* and its salts do not precipitate solutions of aluminium.

10. *Potassium sulphate*, added to very concentrated solutions of salts of

aluminium, occasions the gradual separation, in the form of crystals, or a crystalline powder, of aluminium potassium sulphate.*

11. If aluminium hydroxide or other compound is ignited upon charcoal before the blowpipe, and afterwards moistened with a solution of *cobalt nitrate*, and then again strongly ignited, an unfused mass of a deep SKY-BLUE color is produced, which consists of a compound of the two oxides. The blue color becomes distinct only upon cooling. By candlelight it appears violet. This reaction is to be relied on in a measure only in the case of infusible or difficultly fusible compounds of aluminium pretty free from other metals; it is never quite decisive, since cobalt solution gives a blue color under similar circumstances not only with readily fusible compounds, but also with certain infusible compounds free from aluminium, such as the normal phosphates of the alkali-earth metals.

§ 102.

b. CHROMIUM, CR. 52.2, AND CHROMIC COMPOUNDS.†

1. CHROMIC OXIDE, Cr_2O_3, is a green, CHROMIC HYDROXIDE, a bluish gray-green powder. Chromic hydroxide dissolves readily in acids. The non-ignited chromic oxide dissolves more difficultly, and the ignited chromic oxide is almost altogether insoluble.

2. The CHROMIC SALTS have a green or violet color. Many of them are soluble in water. Most of them dissolve in hydrochloric acid. The solutions exhibit a fine green or a dark violet color, which latter, however, changes to green upon heating. The chromic salts with volatile acids are decomposed upon ignition, the acids being expelled. The chromic salts which are soluble in water redden litmus. Anhydrous chromic chloride is crystalline, violet-colored, insoluble in water and in acids, and volatilizes with difficulty.

3. *Potassa and soda* produce in the green as well as in the violet solutions a bluish-green precipitate of CHROMIC HYDROXIDE which dissolves readily and completely in an excess of the precipitant, imparting to the fluid an emerald-green tint. Upon *long-continued* ebullition of this solution, the whole of the hydroxide separates again, and the supernatant fluid appears perfectly colorless.

The same reprecipitation takes place if ammonium chloride is added to the alkaline solution. Application of heat promotes the separation of the precipitate.

$$* \; Al_2K_2(SO_4)_4 + 24H_2O; \quad \text{or,} \quad \begin{matrix} K>SO_4 \\ Al{-}SO_4 \\ | \\ Al{-}SO_4 \\ K>SO_4 \end{matrix} + 24H_2O.$$

† In the chromic compounds, Cr is apparently trivalent, but is really quadrivalent, Cr_2 being sexivalent, thus:

4. *Ammonia* produces in green solutions a grayish-green, in violet solutions a grayish-blue precipitate of CHROMIC HYDROXIDE.

The former precipitate dissolves in acids to a green fluid, the latter to a violet fluid. Other circumstances (concentration, way of adding the ammonia, etc.) exercise also some influence upon the composition and color of these hydroxides. A small portion of the hydroxide redissolves in an excess of the precipitant in the cold, imparting to the fluid a peach-blossom red tint; but if, after the addition of ammonia in excess, heat is applied to the mixture the precipitation is complete.

5. *Alkali carbonates* precipitate BASIC CHROMIC CARBONATE, which redissolves with difficulty in excess of the precipitant.

6. *Barium carbonate* precipitates the whole of the chromium as a GREENISH HYDROXIDE MIXED WITH BASIC SALT. The precipitation takes place in the cold, but is complete only after long-continued digestion.

N. B. to 3, 4, 5, and 6.—Tartaric and citric acids, sugar, and oxalic acid interfere more or less with the precipitation of violet or green solutions of chromic hydroxide by ammonia, the first formed precipitates frequently redissolving entirely to red fluids after long standing. The above-named acids generally prevent altogether the precipitation by sodium carbonate. In the presence of these acids also the precipitation by barium carbonate is incomplete.

7. If a solution of chromic hydroxide in solution of potassa or soda is mixed with some *lead dioxide* in excess, and the mixture is boiled a short time, the chromic hydroxide is oxidized to chromic acid. A yellow fluid is therefore obtained on filtering which consists of a solution of LEAD CHROMATE in solution of potassa or soda. Upon acidifying this fluid with acetic acid, the lead chromate separates as a yellow precipitate (CHANCEL). Very minute traces of chromic acid may be detected in this fluid with still greater certainty by acidifying with hydrochloric acid, and bringing it in contact with hydrogen dioxide and ether. (Compare § 138.)

8. The fusion of chromic oxide or of any chromic compound with *sodium nitrate and carbonate*, or still better, with *potassium chlorate and sodium carbonate*, gives rise to the formation of yellow ALKALI-CHROMATE, which dissolves in water to an intensely yellow fluid. For the reactions of chromic acid see § 138.

9. *Sodium metaphosphate** dissolves chromic oxide and chromic salts, both in the oxidizing and reducing flame of the blowpipe, to clear beads of a faint yellowish-green tint, which upon cooling change to EMERALD-GREEN. Chromic oxide and chromic salts show a similar reaction with *sodium*

* Obtained by fusing, on platinum wire, hydrogen sodium phosphate. See § 85 *a*.

tetraborate. The Bunsen gas flame is used for the experiment, or the blowpipe flame.

§ 103.

Recapitulation and remarks.—The solubility of aluminium hydroxide in solutions of potassa and soda, and its reprecipitation from the alkaline solutions by ammonium chloride, afford a safe means of detecting aluminium in the absence of chromic salts. But if the latter are present, which is seen either by the color of the sclution, or by the reaction with sodium metaphosphate, they must be removed before aluminium can be tested for.

The separation of chromium from aluminium is effected the most completely by fusing 1 part of the mixed oxides with 2 parts of sodium carbonate and 2 parts of potassium chlorate, which may be done in a platinum crucible. The yellow mass obtained is boiled with water ; by this process the whole of the chromium is dissolved as potassium chromate, and part of the aluminium as potassium aluminate, the rest of the aluminium remaining undissolved. If the solution is acidified with nitric acid, it acquires a reddish-yellow tint ; if ammonia is then added to feebly alkaline reaction, the dissolved portion of the aluminium separates.

The precipitation of chromic hydroxide, effected by boiling its solution in solution of potassa or soda, is also sufficiently exact if the ebullition is continued long enough ; still it is often liable to mislead in cases where only little chromic salt is present, or where the solution contains organic matter, even though in small proportion only. I have to call attention here to the fact that the solubility of chromic hydroxide in an excess of cold solution of potassa or soda is considerably impaired by the presence of other hydroxides (manganous, nickelous and cobaltous hydroxides, and more particularly ferric hydroxide). If these hydroxides happen to be present in large excess they may even altogether prevent the solution of the chromic hydroxide in potassa or soda solution. Lastly, the influence of non-volatile organic acids, sugar, etc., upon the precipitation of aluminium and chromium hydroxides by ammonia, etc., must be remembered. If organic substances are present therefore, ignite, fuse the residue with sodium carbonate and potassium chlorate, and proceed as directed before. In respect to the detection of traces of aluminium by an alcoholic solution of morin, compare GOPPELSRÖDER.*

Special Reactions of the rarer Metals of the Third Group.

§ 104.

1. BERYLLIUM or GLUCINUM, Gl. 9.4.

Beryllium is a rare metal found in the form of a silicate in phenacite, and,

* Zeitschr. f. anal. Chem., 7, 208.

with other silicates, in beryl, euclase, and some other rare minerals. Beryllium oxide (berylla or glucina) is a white, tasteless powder, insoluble in water. The ignited earth dissolves slowly but completely in acids; it is readily soluble after fusion with sodium disulphate. The hydroxide dissolves readily in acids. The compounds of beryllium very much resemble the aluminium compounds. The soluble beryllium salts have a sweet astringent taste; their reaction is alkaline. The native silicates of beryllium are completely decomposed by fusing with 4 parts of sodium carbonate. *Potassa, soda, ammonia,* and *ammonium sulphide* throw down from solution of beryllium salts white flocculent hydroxide, which is insoluble in ammonia, but dissolves readily in solution of potassa or soda, from which solution it is precipitated again by ammonium chloride; the concentrated alkaline solutions remain clear on boiling, but from more dilute alkaline solutions almost the whole of the beryllium separates upon continued ebullition (difference between beryllium and aluminium). Upon continued ebullition with *ammonium chloride*, the freshly precipitated hydroxide dissolves as beryllium chloride, with expulsion of ammonia (difference between beryllium and aluminium). *Alkali carbonates* precipitate white beryllium carbonate, which redissolves in a great excess of sodium or potassium carbonate, and in a much less considerable excess of ammonium carbonate (most characteristic difference between beryllium and aluminium, but they cannot be completely separated in this way, as in the presence of beryllium a certain quantity of aluminium dissolves in ammonium carbonate, Joy). Upon boiling these solutions basic beryllium carbonate separates readily and completely from the solution in ammonium carbonate, but only upon dilution and imperfectly from the solutions in sodium and potassium carbonate. *Barium carbonate* precipitates beryllium completely upon cold digestion. *Oxalic acid* and *oxalates* do not precipitate beryllium (difference between beryllium and thorium, zirconium, yttrium, erbium, cerium (in cerous salts), lanthanium, didymium). Beryllium, when fused with 2 parts of *hydrogen potassium fluoride*, dissolves in water acidified with hydrofluoric acid. (This reaction serves as a means of separating beryllium from aluminium, for when aluminium is similarly treated it remains insoluble as aluminium potassium fluoride.) Moistened with solution of *cobalt nitrate*, the beryllium compounds give gray masses upon ignition.

2. Thorium or Thorinum, Th. 231.

Thorium is a very rare metal, found in thorite and monazite. Thorium oxide (thoria or thorina) is white, while hot, yellow. Ignited thoria is soluble only upon heating with a mixture of 1 part of concentrated sulphuric acid and 1 part of water; but it is not soluble in other acids, not even after fusion with alkalies. When evaporated with hydrochloric or nitric acid, the corresponding salts are left in a varnish-like form, which dissolves at once in water completely. Hydrochloric and nitric acids precipitate from such solutions the chloride or nitrate; even sulphuric acid may produce a precipitate in the solutions (Bahr). The moist hydroxide dissolves readily in acids, the dried hydroxide only with difficulty. Thorium chloride is not volatile. Thorite (thorium silicate) is decomposed by moderately concentrated sulphuric acid, and also by concentrated hydrochloric acid. *Potassa, ammonia,* and *ammonium sulphide* precipitate from solutions of thorium salts white hydroxide, which is insoluble in an excess of the precipitant, even of potassa (difference

between thorium, and aluminium, and beryllium). *Potassium carbonate*, and *ammonium carbonate*, precipitate basic thorium carbonate, which readily dissolves in an excess of the precipitant in concentrated solutions, with difficulty in dilute solutions (difference between thorium and aluminium). From the solution in ammonium carbonate basic salt separates again even at 50°. *Barium carbonate* precipitates thorium completely. *Hydrofluoric acid* precipitates the fluoride, which at first appears gelatinous, but after a little while pulverulent. The precipitate is insoluble in water and hydrofluoric acid. (Here thorium differs from aluminium, beryllium, zirconium, and titanium). *Oxalic acid* produces a white precipitate (here thorium differs from beryllium and aluminium). The precipitate does not dissolve in oxalic acid nor in dilute mineral acids, but it does dissolve in a solution of ammonium acetate containing free acetic acid. (Here thorium differs from yttrium and cerium in cerous salts). The precipitate is insoluble in excess of ammonium oxalate (difference between thorium and zirconium). *Potassium sulphate* in concentrated solution precipitates thorium slowly but completely (here thorium differs from aluminium and beryllium). The precipitate consists of thorium sulphate; it is insoluble in concentrated solution of potassium sulphate, it dissolves with difficulty in cold and also in hot water, but readily on addition of some hydrochloric acid. On heating the neutral solution of thorium sulphate in cold water, it separates in the form of a heavy white curdy precipitate (difference between thorium, and aluminium, and beryllium). This precipitate redissolves in cold water (in which it differs from titanium). *Sodium thiosulphate* precipitates from neutral or slightly acid solutions on boiling thorium thiosulphate mixed with sulphur; the precipitation, however, is not quite complete (difference between thorium and yttrium, erbium and didymium).

3. Zirconium, Zr. 89.6.

Found in zircon and some other rare minerals. Zirconium oxide or zirconia (ZrO_2) is a white powder insoluble in hydrochloric acid, soluble upon addition of water, after continued heating with a mixture of 2 parts of hydrated sulphuric acid and 1 part of water. The hydroxide resembles aluminium hydroxide, dissolving readily in hydrochloric acid when precipitated cold, and still moist, but with difficulty when precipitated hot, or after drying. The zirconium salts soluble in water redden litmus. The native zirconium silicates may be decomposed by fusion with sodium carbonate. The finely elutriated silicate is fused at a high temperature, together with 4 parts of sodium carbonate. The fused mass gives to water sodium silicate, a sandy sodium zirconate being left behind, which is washed, and dissolves in hydrochloric acid. Zircon may easily be decomposed by fusion with hydrogen potassium fluoride at a red heat, potassium silicofluoride and zirconium potassium fluoride being produced. *Potassa, soda, ammonia*, and *ammonium sulphide* precipitate from solutions of zirconium salts a flocculent hydroxide, which is insoluble in an excess of the precipitant, even of soda and potassa (difference between zirconium and aluminium, and beryllium), and is not dissolved even by boiling solution of ammonium chloride (difference between zirconium and beryllium). *Carbonates of potassium, sodium* and *ammonium*, throw down zirconium carbonate as a flocculent precipitate, which redissolves in a large excess of potassium carbonate, more readily in potassium bicarbonate, and most readily in ammonium carbonate (difference between zirconium and aluminium), from which

solution it precipitates again on boiling. *Oxalic acid* produces a bulky precipitate of zirconium oxalate (difference between zirconium and aluminium and beryllium), which is soluble in oxalic acid, soluble in hydrochloric acid, soluble in excess of ammonium oxalate (difference between zirconium and thorium). A concentrated solution of *potassium sulphate* speedily produces a white precipitate of zirconium potassium sulphate, insoluble in excess of the precipitant (difference between zirconium and aluminium and beryllium), which—if precipitated cold—dissolves readily in a large proportion of hydrochloric acid, but is almost absolutely insoluble in water and in hydrochloric acid if precipitated hot (difference between zirconium and thorium and cerium in cerous salts). Zirconium sulphate is difficultly soluble in cold water, readily soluble in hot water (difference between zirconium and thorium). *Barium carbonate* does not precipitate zirconium salts completely, even upon boiling. *Hydrofluoric acid* does not precipitate zirconium salts (difference between zirconium and thorium and yttrium). *Sodium thiosulphate* precipitates zirconium salts (difference between zirconium and yttrium, erbium and didymium). The separation of the zirconium thiosulphate takes place on boiling even in the presence of 100 parts of water to 1 part of the metal (difference between zirconium and cerium and lanthanium). *Turmeric paper* dipped into solutions of zirconium slightly acidified with hydrochloric or sulphuric acid, acquires a brownish-red color after drying (difference between zirconium and thorium). In the presence of titanic acid, which also has the effect of turning turmeric paper brown, treat the acid solution with zinc first, to reduce the titanic acid to titanous oxide, the solution of which does not affect turmeric paper (PISANI).

4. YTTRIUM, Y. 61.7.

Yttrium is a rare metal found in gadolinite, orthite, yttro-tantalite. Yttria (Y O) when pure is pale yellowish white, when ignited in the oxidizing flame it emits a white light (difference between yttrium and erbium) without fusing or volatilizing. In nitric, hydrochloric, and dilute sulphuric acid it is difficultly soluble in the cold, but on warming it dissolves completely after some time. The solutions, and likewise the salts of yttrium are colorless; they have an acid reaction and a sweetish astringent taste. Yttria does not combine directly with water. Yttrium under no circumstances yields a spectrum, nor do the solutions of its salts show any absorption bands (BAHR and BUNSEN). Anhydrous yttrium chloride is not volatile (difference between yttrium and aluminium, beryllium and zirconium). *Potassa* precipitates white hydroxide, which is insoluble in an excess of the precipitant (difference between yttrium and aluminium and beryllium). *Ammonia* and *ammonium sulphide* produce the same reaction. Presence of a small quantity of ammonium chloride will not prevent the precipitation by ammonium sulphide; but in presence of a large excess of ammonium chloride, ammonium sulphide fails to precipitate solutions of yttrium salts. *Alkali carbonates* produce a white precipitate, which dissolves with difficulty in potassium carbonate, but more readily in hydrogen potassium carbonate and in ammonium carbonate, though by no means so readily as the corresponding beryllium precipitate. The solution of the pure hydroxide in ammonium carbonate deposits on boiling the whole of the yttrium; if ammonium chloride is present at the same time, this is decomposed upon continued heating, with separation of ammonia, and the pre-

cipitate redissolves as yttrium chloride. Saturated solutions of yttrium carbonate in ammonium carbonate have a tendency to deposit yttrium carbonate, which should be borne in mind. *Oxalic acid* produces a white precipitate (difference between yttrium and aluminium and beryllium). The precipitate does not dissolve in oxalic acid, but it dissolves with difficulty in dilute hydrochloric acid, and it is partially dissolved by boiling with ammonium oxalate. *Yttrium potassium sulphate* dissolves readily in water and in solution of potassium sulphate (difference between yttrium and thorium, zirconium and the metals of cerite). *Barium carbonate* produces no precipitate in the cold (difference between yttrium and aluminium, beryllium, thorium, cerium, and didymium), on boiling even the precipitation is incomplete. *Turmeric paper* is not altered by acidified solutions of yttrium salts (difference between yttrium and zirconium). *Tartaric acid* does not interfere with the precipitation of yttrium by alkalies (characteristic difference between yttrium and aluminium, beryllium, thorium and zirconium). The precipitate is yttrium tartrate. The precipitation ensues only after some time, but it is complete. *Sodium thiosulphate* does not precipitate yttrium (difference between yttrium and aluminium, thorium, zirconium and titanium). *Hydrofluoric acid* produces a precipitate (here yttrium differs from aluminium, beryllium, zirconium and titanium); the precipitate is gelatinous, insoluble in water and hydrofluoric acid; before ignition it will dissolve in mineral acids, after ignition it is decomposed only by strong sulphuric acid. A cold saturated solution of the *sulphate becomes turbid when heated* to between 30° and 40°; on boiling almost the whole of the salt separates. Yttrium gives clear colorless beads with *borax* and *sodium metaphosphate* in both the outer and inner flame (difference between yttrium and cerium and didymium).

5. Erbium, Er. 112.6.

Erbium accompanies yttrium in gadolinite.* Erbium oxide is distinguished by its fine rose color, it does not alter on ignition in hydrogen, and does not fuse in the highest white heat. When strongly heated in the form of a spongy mass, it glows with an intense green light. In *nitric, hydrochloric,* and *sulphuric acid* it dissolves with difficulty, but on warming completely. The *erbium salts* have a more or less bright rose tint, which is stronger generally with the hydrated than with the anhydrous salts; they have an acid reaction and a sweetish astringent taste. Erbium oxide does not combine directly with water. The sulphate when hydrated dissolves in water with difficulty, when anhydrous it dissolves readily. The basic nitrate (NO_3. Er . O H + H_2 O) forms bright rose-colored, needle-shaped crystals which are difficultly soluble in nitric acid, decomposed by water into nitric acid and gelatinous hyperbasic salt, and yield the oxide on ignition. The oxalate is a rose-colored, heavy sandy powder. Finally the erbium oxide is most decisively characterized by the *absorption spectrum* which is given by the solutions of its salts. Of the absorption bands α lies between 71 and 74, β between 64.5 and 65.5, γ between 32.6 and 38.0, δ between 85 and 91 on the spectrum plate.

* Mosander imagined that he had separated also another element, terbium. Popp considered both erbium and terbium to be mixtures of yttrium with cerium and didymium. Delafontaine defended Mosander's view. However, Bahr and Bunsen found in gadolinite, besides yttrium, only erbium (Annal. d. Chem. u. Pharm., 137, 1).

If the ignited oxide is saturated with not too concentrated phosphoric acid and reignited, a direct spectrum is obtained, the bright lines of which coincide with the dark ones of the absorption-spectrum. With *borax* and *sodium metaphosphate* erbium gives beads which are clear and colorless when hot, and also after cooling (difference between erbium and cerium and didymium).

In the separation of erbium from yttrium, which show a great likeness to each other in their deportment to reagents, BAHR and BUNSEN make use of the different behavior of the nitrates when heated. The separation is, however, not complete unless the process is repeated over and over again. Compare *op. cit.*, p. 3.

6. CERIUM, Ce. 92.

Cerium is found in cerite, orthite, etc. It forms two oxides, cerous oxide (Ce O) and ceric oxide ($Ce_2 O_4$), The cerous hydroxide is white, but turns yellow upon exposure to the air, by absorption of oxygen. By ignition in the air it is converted into orange-red or red ceric oxide (difference between it and the preceding elements of the 3d group). Cerous hydroxide dissolves readily in acids. Ignited ceric oxide, containing lanthanium and didymium monoxides, dissolves readily in hydrochloric acid, with evolution of chlorine ; in the pure state it dissolves very slightly in boiling hydrochloric acid ; upon addition of alcohol it passes into solution (difference between cerium and thorium and zirconium) ; the solution contains cerous chloride. Ceric oxide dissolves in concentrated sulphuric acid, although with difficulty ; it is hardly attacked by nitric acid. The ceric oxide obtained from the oxalate when evaporated with nitric acid yields a basic salt, which gives an emulsion with water, and is not completely soluble in very considerable quantities of water (difference from thorium). The cerous salts are colorless, occasionally with a slight shade of amethyst-red ; the soluble cerous salts redden litmus. Cerous chloride is not volatile (difference from aluminium, beryllium, and zirconium). The sulphate does not dissolve entirely in boiling water. Cerite does not dissolve in aqua regia, but is decomposed by fusion with sodium carbonate, and also by concentrated sulphuric acid. *Potassa* precipitates white hydroxide, which turns yellow in the air, and does not dissolve in an excess of the precipitant (difference from aluminium and beryllium). *Ammonia* precipitates basic salt, which is insoluble in an excess of the precipitant. *Alkali carbonates* produce a white precipitate, which dissolves sparingly in an excess of potassium carbonate, somewhat more readily in ammonium carbonate. *Oxalic acid* produces a white precipitate ; the precipitation is complete even in moderately acid solutions (difference from aluminium and beryllium). The precipitate is not dissolved by oxalic acid, but it dissolves in a large proportion of hydrochloric acid. A saturated solution of *potassium sulphate* precipitates, even from somewhat acid solutions, white cerous potassium sulphate (difference from aluminium and beryllium), which is difficultly soluble in cold water, readily soluble in hot water and altogether insoluble in a saturated solution of potassium sulphate (difference from yttrium). The precipitate may be dissolved by boiling with a large quantity of water, to which some hydrochloric acid has been added. *Barium carbonate* precipitates solutions of cerium salts slowly, but completely upon long-continued action. *Tartaric acid* prevents precipitation by ammonia (difference from yttrium) but not by potassa. *Sodium thiosulphate* does not precipitate cerium, even on boiling with very concentrated

solutions. The precipitated sulphur only carries down traces of the salt with it. If we conduct *chlorine* through a not too acid solution of a cerous salt mixed with sodium acetate, or if we add *sodium hypochlorite* to such a solution, all the cerium is precipitated as a light yellow ceric hydroxide (free from didymium and lanthanium. POPP). If a cerous salt be dissolved in nitric acid, with addition of an equal volume of water, and if a small quantity of *lead dioxide* be added, and the liquid be boiled for some minutes, the solution turns yellow, even if only small quantities of cerium be present. On evaporating this solution to dryness, heating the residue till a portion of the acid escapes, and treating it with water acidified with nitric acid, no cerium will be dissolved, but any didymium and lanthanium present will be dissolved (GIBBS). Solutions of ceric salts are precipitated in the cold by *barium carbonate*. *Sodium thiosulphate* precipitates a solution of ceric nitrate. *Borax* and *sodium metaphosphate* dissolve cerium oxides in the outer flame to yellowish red beads (difference from the preceding metals); the coloration gets fainter on cooling, and often disappears altogether. In the inner flame colorless beads are obtained.

7. LANTHANIUM, La. 93.6.

This element is generally found associated with cerium. Lanthanium oxide is white and remains unaltered by ignition in the air (difference from cerous oxide). In contact with cold water it is slowly converted into a milk-white hydroxide; with hot water the conversion is rapid. The oxide and hydroxide change the color of reddened litmus-paper to blue; they dissolve in boiling solution of ammonium chloride, also in dilute acids. Lanthanium oxide in this resembles magnesia. The salts of lanthanium are colorless; the saturated solution of lanthanium sulphate in cold water deposits a portion of the salt already at 30° (difference from cerium). *Potassium sulphate, oxalic acid,* and *barium carbonate* give the same reactions as with cerous salts. *Potassa* precipitates hydroxide, which is insoluble in an excess of the precipitant, and does not turn brown in the air. *Ammonia* precipitates basic salts, which pass milky through the filter on washing. The precipitate produced by ammonium carbonate is insoluble in an excess of the precipitant (difference from cerous salts). If a cold dilute solution of lanthanium acetate is supersaturated with ammonia, the slimy precipitate repeatedly washed with cold water, and a little *iodine* in powder added, a blue coloration makes its appearance, which gradually pervades the entire mixture (characteristic difference between lanthanium and the other earth metals).

8. DIDYMIUM, D. 95.

This element, like lanthanium and in conjunction with it, is found associated with cerium. Didymium oxide after intense ignition appears white, moistened with nitric acid and feebly ignited dark brown, after intense ignition again white. In contact with water it is slowly converted into hydroxide; it rapidly attracts carbon dioxide; its reaction is not alkaline; it dissolves readily in acids. The concentrated solutions have a reddish or a faint violet color. The nitrate on heating is first converted into a basic salt (difference from lanthanium) which is gray when hot and also when cold (difference from erbium). The chloride is not volatile. The saturated solu-

tion of the sulphate deposits salt, not at 80°, but upon boiling. *Potassa* precipitates hydroxide, which is insoluble in an excess of the precipitant, and does not alter in the air. *Ammonia* precipitates basic salt, which is insoluble in ammonia, but slightly soluble in ammonium chloride. *Alkali carbonates* produce a copious precipitate, which is insoluble in an excess of the precipitant, even in an excess of ammonium carbonate (difference from cerous salts), but dissolves slightly in concentrated solution of ammonium chloride. *Oxalic acid* precipitates salts of didymium almost completely; the precipitate is difficultly soluble in cold hydrochloric acid, but dissolves in that menstruum upon application of heat. *Barium carbonate* precipitates didymium solutions slowly (more slowly than cerous and lanthanium solutions), and never completely. A concentrated solution of *potassium sulphate* precipitates didymium solutions more slowly and less completely than cerous solutions. The precipitate is insoluble in solution of potassium sulphate and in water (DELAFONTAINE), but it dissolves in hot hydrochloric acid with difficulty. *Sodium thiosulphate* does not precipitate solutions of didymium. Didymium gives with *borax* in both flames a nearly colorless bead, which in the presence of large quantities has a faint amethyst-red tinge. *Sodium metaphosphate* dissolves the oxide in the reducing flame to an amethyst-red bead inclining to violet. With *sodium carbonate* in the outer flame a grayish-white mass is obtained (difference from manganese). The *absorption spectrum* given by the solutions of the salts is peculiarly characteristic for didymium. This was first described by GLADSTONE, and afterwards by O. L. ERDMANN and DELAFONTAINE. BAHR and BUNSEN have laid down the exact position of the bands (Zeitschr. f. anal. Chem., 5, 110). A direct spectrum may also be obtained from didymium as from erbium, but it is by no means well marked.

For the separation of cerium from lanthanium and didymium, one of the following methods may be used :—*a*. Nearly neutralize the solution of the three metals, if acid, without allowing any permanent precipitate to form, add a sufficient quantity of sodium acetate and an excess of sodium hypochlorite, and boil for some time; the cerium will fall as ceric oxide, while lanthanium and didymium remain in solution. (POPP, Ann. d. Chem. u. Pharm.,131, 360.) *b*. Precipitate the metals with potassa, wash, suspend the precipitate in potassa, and pass chlorine. Lanthanium and didymium dissolve; ceric oxide remains behind. (DAMOUR and ST. CLAIRE DEVILLE, Compt. Rend., 59, 272). *c*. Dissolve in a large excess of nitric acid; boil with lead dioxide; evaporate the orange-colored solution to dryness, and heat the residue till a portion of the acid escapes; treat with water acidulated with nitric acid, and separate the insoluble basic ceric nitrate from the solution which contains all the lanthanium and didymium. (GIBBS, Zeitschr. f. anal. Chem., 3, 396.) In using the last method, before proceeding with the residue or solution, the lead must be first separated by hydrogen sulphide. *d*. Heat the chromates to 110°, and treat with hot water to extract the undecomposed compounds of lanthanium and didymium. The cerium remains behind as insoluble ceric oxide (PATTINSON and CLARK, Chem. News, 16, 259). From the solution of lanthanium and didymium obtained by one or the other of the above methods, the bases are precipitated with ammonium oxalate, the oxalates are ignited, and the oxides thus obtained are treated with dilute nitric acid. If the separation of cerium was incomplete, the remainder of the cerium will here remain behind. The solution is evaporated in a dish with a flat

bottom to dryness and heated to 400°–500°. The salts fuse; nitrous fumes escape. The residue is treated with hot water, which dissolves the lanthanium, leaving behind gray basic didymium nitrate. By a repetition of the evaporation, etc., the two bases may be satisfactorily separated. (Damour and St. Claire Deville.) Another method of separation, which is, however, less complete, consists in converting the didymium and lanthanium into sulphates, making a saturated solution of the dry salts in water at 5° or 6°, and heating the solution to 30°, when the lanthanium sulphate is for the most part thrown down and the didymium sulphate is for the most part held in solution. For another method of separating lanthanium and didymium, which requires the presence of a considerable quantity of cerium, compare Cl. Winkler) Zeitschr. f. anal. Chem., 4, 417).

9. Titanium, Ti. 50.

Titanium forms two oxides, titanious oxide (Ti_2O_3) and titanic oxide ($Ti O_2$), and the hydroxides, titanic and metatitanic acids. The latter are more frequently met with in analysis. Titanic oxide is found in the free state in rutile and anatase, in combination with bases in titanite, titaniferous iron, etc. It is found in small proportions in many iron ores, in clays, and generally in silicates, consequently also in blast furnace slags. The small copper-colored cubes which are occasionally found in such slags consist of a combination of titanium cyanide with titanium nitride. Feebly ignited titanic oxide is white; it transiently acquires a lemon tint when heated; very intense ignition gives a yellowish or brownish tint to it. It is infusible, insoluble in water, and its specific gravity is 3.9 to 4.25. The titanic chloride ($Ti Cl_4$) is a colorless volatile fluid, fuming strongly in the air.

a. Deportment with acids, and reactions of acid solutions of titanic oxide.— Ignited titanic oxide is insoluble in acids, except in hydrofluoric acid and in concentrated sulphuric acid. If the solution in hydrofluoric acid is evaporated with sulphuric acid, no titanic fluoride will volatilize (difference from silicic oxide). With sodium sulphate it gives upon sufficiently long continued fusion a clear mass, which is completely soluble in a large proportion of cold water. Titanic oxide is very easily brought into a clear solution, by fusing with hydrogen potassium fluoride and dissolving the fusion in dilute hydrochloric acid. The titanium potassium fluoride is difficultly soluble in water, 1 part requiring 90 parts at 14°. Normal titanic hydroxide, $Ti(OH)_4$, or titanic acid, dissolves both moist and when dried without the aid of heat, in dilute acids, especially in hydrochloric and sulphuric acids. All the solutions of titanic acid in hydrochloric or sulphuric acid, but more particularly the latter, when subjected in a highly dilute state to *long-continued boiling*, deposit metatitanic acid as a white powder insoluble in dilute acids. Presence of much free acids retards the separation and diminishes the quantity of the precipitate. The precipitate which separates from the hydrochloric acid solution may, indeed, be filtered, but it will pass milky through the filter on washing, except an acid or ammonium chloride be added to the washing water. *Solution of potassa* throws down from solutions of titanic acid in hydrochloric or sulphuric acid, titanic acid as a bulky white precipitate, which is insoluble in an excess of the precipitant; *ammonia, ammonium sulphide* and *barium carbonate* act in the same way. The precipitate, thrown down cold and washed with cold water, is soluble in hydrochloric acid and in dilute sulphuric acid; presence

of tartaric acid prevents its formation. *Potassium ferrocyanide* produces in acid solutions of titanic acid a dark brown precipitate; *infusion of galls* a brownish precipitate, which speedily turns orange red. On boiling a solution of titanic acid with *sodium thiosulphate*, the whole of the titanic acid is thrown down. *Sodium phosphate* throws down the titanic acid almost completely as phospho-titanic acid, even from solutions containing much hydrochloric acid. The washed precipitate consists of $P_2 Ti_2 O_7$ (MERZ). *Zinc* or *tin* boiled in acid titanic solutions produces after some time a pale violet or blue coloration; subsequently a blue precipitate, which gradually becomes white. The coloration is caused by the reduction of the titanic acid to titanous hydroxide. If to the blue but still clear solution potassa or ammonia is added, blue titanous hydroxide separates, which is gradually converted into white titanic acid with decomposition of water. The reduction of titanic acid in hydrochloric solution takes place also in the presence of potassium fluoride (difference from niobic acid), the fluid becoming bright green. The solutions of titanium chloride in water have properties which vary according to their preparation with hot or cold water. The solution prepared with cold water is not precipitated by sulphuric acid, nor by hydrochloric, nor by nitric, it is precipitated by phosphoric acid, arsenic acid, or iodic acid; but if the solution be boiled only for a few seconds it becomes slightly opalescent, and so far modified that hydrochloric and nitric acids produce white precipitates in it which are insoluble in excess of the acids, sulphuric acid also precipitates it, but an excess redissolves the precipitate. The solution prepared in the cold contains titanic acid, the boiled solution contains metatitanic acid. (R. WEBER, Pogg. Ann., 120, 287.)

b. Reaction with alkalies.—Recently precipitated titanic acid is almost absolutely insoluble in solution of potassa. If titanic oxide or acid is fused with *hydrate of potassa*, and the fused mass treated with water, the solution contains a little more titanic acid. By fusion with *alkali carbonates* normal alkali titanates are formed, with expulsion of carbon dioxide. Water extracts from the fused mass alkali and alkali carbonate, leaving behind acid titanate of the alkali metal, soluble in hydrochloric acid.

Titanic oxide mixed with charcoal gives, upon ignition in a *stream of chlorine*, titanium chloride as a volatile liquid, which emits copious fumes in the air. *Sodium metaphosphate* dissolves titanic oxide at the point of the outer blowpipe flame to a colorless bead but with difficulty, in the outer flame but near the point of the inner flame it dissolves readily and in considerable quantity. If the clear and colorless bead is again held in the point of the outer flame, it becomes opaque if sufficiently saturated, and by continued action of the flame titanic oxide will separate in microscopic crystals of the form of anatase (G. ROSE). If the bead is held in a good reducing flame for some time, it will appear yellow while hot, red while cooling, and violet when cold. The reduction is promoted by the addition of a little tin. If some ferrous sulphate is added, the bead obtained in the reducing flame will appear blood-red.

10. TANTALUM, Ta. 182.*

Tantalum forms with oxygen tantalic oxide, $Ta_2 O_5$. There is also a tanta-

* The results of the recent investigations on tantalum and niobium by MARIGNAC, BLOMSTRAND, DEVILLE, and TROOST, and HERMANN will be found in Zeitschr. f. anal. Chem., 5, 384 *et seq.*, and 7, 104 *et seq.*

lous oxide, Ta O_2. Tantalum occurs in columbite and tantalite (almost always in conjunction with niobium). Tantalic oxide is white, pale yellowish when hot (difference from Ti O_2). It has a specific gravity of 7.6–8.01. Tantalic oxide is not reduced by ignition in a current of *hydrogen*. It combines with acids as well as with bases.

a. Acid solutions.—When tantalic oxide is intimately mixed with charcoal and ignited in a current of dry *chlorine*, tantalum chloride (Ta Cl_5) is formed. The latter is yellow, solid, fusible, and can be sublimed ; it is decomposed by water, with separation of tantalic acid (hydroxide) ; it is entirely soluble in sulphuric acid, nearly so in hydrochloric acid, and partially soluble in potassa solution. If titanium is present, on treating the mixtures of oxides and charcoal with a current of chlorine, titanium chloride will be formed and will fume strongly in the air. Tantalic acid dissolves in *hydrofluoric acid*, the solution, when mixed with potassium fluoride, yields a very characteristic salt in fine needles (2 K F . Ta F_5), which is distinguished by its difficult solubility in water acidified with hydrofluoric acid (1 of the acid to 150 or 200 of water). Hydrochloric and concentrated sulphuric acid do not dissolve ignited tantalic oxide. With sodium disulphate it fuses to a colorless mass ; if this is treated with water, tantalic acid combined with sulphuric acid remains undissolved (difference between tantalic acid and titanic acid, but cannot be made the ground of a method of separation). When ignited in an atmosphere of ammonium carbonate, the tantalic sulphate is converted into tantalic oxide. If a solution of alkali tantalate is mixed with hydrochloric acid in excess, the first-formed precipitate redissolves to an opalescent fluid. *Ammonia* and *ammonium sulphide* precipitate from this fluid tantalic acid or an acid ammonium tantalate, but tartaric acid prevents the precipitation. *Sulphuric acid* precipitates tantalic sulphate from the opalescent fluid. When acid solutions of tantalic acid are brought into contact with *zinc*, no blue coloration is observed (difference between tantalic acid and niobic acid).

b. Behavior to alkalies.—By continued fusion with *potassium hydroxide* potassium tantalate is formed ; the fused mass dissolves in water. By fusion with *sodium hydroxide* a turbid mass is obtained ; a little water poured on this mass will dissolve out the excess of sodium hydroxide, leaving the whole of the sodium tantalate undissolved, as this latter salt is insoluble in solution of soda ; but the sodium tantalate will dissolve in water after the removal of the excess of soda. Solution of soda throws down from this solution the sodium tantalate ; if the precipitant be added slowly, the form of the precipitate is crystalline. Carbon dioxide throws down from solutions of alkali tantalates acid salts not soluble in boiling solution of sodium carbonate. *Sulphuric acid* throws down tantalic sulphate even from the dilute solutions of alkali tantalates ; *potassium ferrocyanide* and *infusion of galls* produce precipitates only in acidified solutions ; the precipitate produced by the former is yellow, by the latter light brown.

Sodium metaphosphate dissolves tantalic acid and oxide to a colorless bead, which is colorless also when hot, remains colorless even in the inner flame, and does not acquire a blood-red tint by addition of ferrous sulphate (difference between tantalum and titanium).

11. Niobium, Nb. 94.

Niobium combines with oxygen in several proportions, viz., Nb O, Nb O_2,

and $Nb_2 O_5$. It is occasionally found in columbite, samarskite, etc., and it is usually accompanied by tantalum. Niobic oxide ($Nb_2 O_5$) is white, but turns transiently yellow when ignited (difference between niobic oxide and tantalic oxide). Its specific gravity lies between 4.37 to 4.53 (difference between niobic oxide and tantalic oxide). By strong ignition in *hydrogen* the niobic oxide is converted into black $Nb O_2$. Niobic oxide combines both with bases and acids. Niobic acid (hydroxide) is a white, bulky, insoluble precipitate.

a. Acid solutions of niobium.—Concentrated *sulphuric acid* dissolves the acid on heating, unless it has been strongly ignited and thus converted into oxide. On the addition of much cold water, a clear solution is obtained. On fusing with *sodium* or *potassium disulphate*, both acid and oxide dissolve readily to a colorless mass, and on treating the fusion with boiling water niobic acid containing sulphuric acid remains undissolved, which however is readily soluble in hydrofluoric acid (see below). By mixing niobic oxide intimately with charcoal and treating with a current of *chlorine*, a mixture is obtained of white infusible difficultly volatile niobic oxychloride ($Nb O Cl_3$) and yellow more volatile niobic chloride ($Nb Cl_5$). Treated with water both compounds give turbid fluids, in which a portion of the niobium is separated as niobic acid, but the larger portion remains dissolved. By boiling with hydrochloric acid and afterwards adding water the compounds give clear solutions, which are not precipitated by boiling or by sulphuric acid in the cold (difference from tantalum chloride). By igniting niobic oxide in the vapor of niobium chloride the oxychloride is formed (difference from tantalic oxide). From the acid solutions of niobium, *ammonia* and *ammonium sulphide* throw down niobic acid containing ammonia; this dissolves in *hydrofluoric acid*. The hydrofluoric solution when mixed with potassium fluoride gives potassium niobium fluoride ($2 K F . Nb F_5$) when hydrofluoric acid is in excess, otherwise it gives potassium niobium oxyfluoride ($2 K F . Nb O F_3$). The latter salt is also obtained when potassium niobate is dissolved in hydrofluoric acid; it is readily soluble in cold water, one part dissolving in 12.5 parts (difference from potassium titanium fluoride, which requires 96 parts of water, and from potassium tantalum fluoride, which requires 200 parts of water). On digesting a hydrochloric or sulphuric acid solution of niobic acid with *zinc* or *tin*, it acquires a blue and generally also a brown color, in consequence of the reduction of the niobic acid to lower hydroxides. In the presence of alkali fluorides the reduction does not take place (difference between niobic acid and titanic acid).

b. Alkaline solutions.—With *potassium hydroxide* niobic oxide or acid fuses to a clear mass, soluble in water. To *sodium hydroxide* niobic oxide or acid shows the same deportment as tantalic acid or oxide. From the solution of potassium niobate, solution of *soda* precipitates an almost insoluble sodium niobate. On boiling a solution of potassium niobate with *potassium hydrogen carbonate* an almost insoluble acid potassium niobate is thrown down. On fusing niobic acid or oxide with *sodium carbonate* and boiling the fusion with water, a crystalline acid sodium niobate remains undissolved. *Carbon dioxide* when passed into solution of sodium niobate precipitates all the niobic acid as an acid salt.

Sodium metaphosphate dissolves niobic acid or oxide readily; the bead held in the outer flame appears colorless as long as it is hot; in the inner flame it has a violet, blue, or brown color, according to the quantity of the acid present, and a red color on the addition of ferrous sulphate.

For the best methods of detecting the whole of the members of the third group in presence of each other, see Part II., Section III.

§ 105.

FOURTH GROUP.

More common metals :—ZINC, MANGANESE, NICKEL, COBALT IRON.

Rarer elements :—URANIUM, THALLIUM, INDIUM, VANADIUM.

Properties of the Group.—The solutions of the metals of the fourth group, if containing a stronger free acid, are not precipitated by hydrogen sulphide; nor are neutral solutions, at least not completely. But alkaline solutions are completely precipitated by hydrogen sulphide; and so are other solutions if a sulphide of an alkali metal is used as the precipitant, instead of hydrogen sulphide.* The precipitated sulphides are insoluble in water; some of them are readily soluble in dilute acids; others (nickel sulphide and cobalt sulphide) dissolve only with very great difficulty in these menstrua. Some of them are insoluble in sulphides of the alkali metals, others (nickel) are sparingly soluble in them, under certain circumstances, whilst others again (vanadium) are completely soluble. The metals of the fourth group differ accordingly from those of the first and second group in this, that their solutions are precipitated by ammonium sulphide, and from those of the third group inasmuch as the precipitates produced by ammonium sulphide are sulphides, and not hydroxides, as is the case with aluminium, chromium, etc.

Special Reactions of the more common Metals of the Fourth Group.

§ 106.

a. ZINC, Zn. 65.2.

1. METALLIC ZINC is bluish white and very bright; when exposed to the air, a thin coating of basic zinc carbonate forms on its surface. It is of medium hardness, malleable at a temperature of between 100° and 150°, but otherwise more or less brittle; it fuses readily on charcoal before the blowpipe, boils afterwards, and burns with a bluish-green flame, giving off white fumes, and coating the charcoal support with oxide. Zinc dissolves in dilute hydrochloric and sulphuric acids, with evolution of hydrogen gas; in dilute nitric

* Vanadic acid behaves in a peculiar way to ammonium sulphide, see § 113, *d*.

acid, with evolution of nitrogen monoxide; in more concentrated nitric acid, with evolution of nitrogen dioxide.

2. ZINC OXIDE and ZINC HYDROXIDE are white powders, which are insoluble in water, but dissolve readily in hydrochloric, nitric, and sulphuric acids. Zinc oxide acquires a lemon-yellow tint when heated, but it resumes its original white color upon cooling. When ignited before the blowpipe, it shines with considerable brilliancy.

3. The ZINC SALTS are colorless; part of them are soluble in water, the rest in acids. The normal salts of zinc which are soluble in water redden litmus paper, and are readily decomposed by heat, with the exception of zinc sulphate, which can bear a dull red heat without undergoing decomposition. Zinc chloride is volatile at a red heat.

4. *Hydrogen sulphide* precipitates from neutral solutions a portion of the metal as white hydrated ZINC SULPHIDE ($ZnS.H_2O$). In acid solutions this reagent fails altogether to produce a precipitate if the free acid present is one of the stronger acids; but from a solution of zinc in acetic acid it throws down the whole of the zinc, even if the acid is present in excess.

5. *Ammonium sulphide* throws down from neutral, and hydrogen sulphide from alkaline solutions, the whole of the metal as hydrated ZINC SULPHIDE, in the form of a white precipitate. Ammonium chloride greatly promotes the separation of the precipitate. From very dilute solutions the precipitate separates only after long standing. This precipitate is not redissolved by an excess of ammonium sulphide, nor by potassa or ammonia; but it dissolves readily in hydrochloric acid, nitric acid, and dilute sulphuric acid. It is insoluble in acetic acid.

6. *Potassa and soda* throw down ZINC HYDROXIDE ($Zn(OH)_2$), in the form of a white gelatinous precipitate, which is readily and completely redissolved by an excess of the precipitant. Upon boiling these alkaline solutions they remain, if concentrated, unaltered; but from dilute solutions nearly the whole of the zinc hydroxide separates as a white precipitate.

Ammonium chloride, added to alkaline solutions not containing a large excess of potassa or soda, produces a white precipitate of zinc hydroxide, which however redissolves on addition of more ammonium chloride (difference between zinc and aluminium).

7. *Ammonia* also produces in solutions, if they do not contain a large excess of free acid, a precipitate of ZINC HYDROXIDE, which readily dissolves in an excess of the precipitant.

The concentrated solution turns turbid when mixed with water. On boiling the concentrated solution, part of the zinc hydroxide separates immediately; on boiling the dilute solution, all the zinc hydroxide precipitates. Ammonium salts interfere with these precipitations more or less.

8. *Sodium carbonate* produces a precipitate of BASIC ZINC CARBONATE, $2\,(Zn\,CO_3) + 3\,Zn\,(O\,H)_2 + 4\,H_2O$, which is insoluble in an excess of the precipitant. Presence of ammonium salts in great excess prevents the formation of this precipitate.

9. *Ammonium carbonate* also produces a precipitate of BASIC ZINC CARBONATE; but this precipitate redissolves upon further addition of the precipitant. On boiling the dilute solution, zinc hydroxide precipitates. Ammonium salts interfere with this precipitation more or less.

N.B. Non-volatile organic acids more or less interfere with the precipitation of solutions of zinc, by the caustic and carbonated alkalies. Sugar does not prevent the precipitations.

10. *Barium carbonate* fails to precipitate solutions of zinc salts in the cold, with the exception of the sulphate.

11. *Potassium ferrocyanide* throws down ZINC FERROCYANIDE ($Zn_3\,Fe\,Cy_6$) as a white slimy precipitate, somewhat soluble in excess of the precipitant, insoluble in hydrochloric acid.

12. *Potassium ferricyanide* throws down ZINC FERRICYANIDE ($Zn_3\,Fe_2\,Cy_{12}$) as a brownish orange-yellow precipitate, soluble in hydrochloric acid and in ammonia.

13. If a mixture of a zinc compound with *sodium carbonate* is exposed to the *reducing flame* of the blowpipe, the charcoal support becomes covered with a slight coating of ZINC OXIDE, which presents a yellow color whilst hot, and turns white upon cooling. This coating is produced by the reduced metallic zinc volatilizing at the moment of its reduction, and being reoxidized in passing through the outer flame. The METALLIC INCRUSTATION obtained according to p. 33 is black with a brown edge, the INCRUSTATION OF OXIDE is white, and therefore invisible upon porcelain. It may be dissolved in nitric acid and examined according to 14.

14. If zinc oxide or one of the zinc salts is moistened with solution of *cobalt nitrate*, and then heated before the blowpipe, an unfused mass is obtained of a beautiful GREEN color; this mass is a compound of zinc oxide with cobalt oxide. If therefore in the first experiment described in 13 the charcoal is moistened around the little cavity with cobalt solution, the coating appears *green when cold*. This test may be applied

with great delicacy by mixing the solution to be tested with a very little of the cobalt solution (not enough to give a bright red color), adding sodium carbonate in slight excess, boiling, filtering off, washing, and igniting on platinum foil. On triturating the residue the green color may be distinctly and readily observed (BLOXAM).

§ 107.

b. MANGANESE,* Mn. 55.

1. METALLIC MANGANESE is whitish-gray, dull, very hard, brittle, and fuses with very great difficulty. It oxidizes rapidly in the air, and in water with evolution of hydrogen, and crumbles to a dark gray powder. It dissolves readily in acids, forming manganous salts.

2. MANGANOUS OXIDE (Mn O) is light green; manganous hydroxide (Mn $(O H)_2$) is white. The former smoulders to brown manganic oxide ($Mn_2 O_3$) when heated in the air, the latter even at the ordinary temperature rapidly absorbs oxygen from the air and passes into brown manganic hydroxide ($Mn(OH)_3$). They are readily soluble in hydrochloric, nitric, and sulphuric acids. All the HIGHER OXIDES OF MANGANESE without exception dissolve to manganous chloride, with evolution of chlorine, when heated with hydrochloric acid; to manganous sulphate, with evolution of oxygen, when heated with concentrated sulphuric acid.

3. The MANGANOUS SALTS are colorless or pale red; part of them are soluble in water, the rest in acids. The salts soluble in water are readily decomposed by a red heat, with the exception of the sulphate. The solutions do not alter vegetable colors.

4. *Hydrogen sulphide* does not precipitate acid solutions; neutral solutions also it fails to precipitate, or precipitates them only very imperfectly.

5. *Ammonium sulphide* throws † down from neutral, and hydrogen sulphide from alkaline solutions, the whole of the metal as hydrated MANGANOUS SULPHIDE ($Mn S . H_2O$), in form of a light flesh-colored † precipitate, which acquires a dark-brown color in the air; this precipitate is insoluble in ammonium sulphide and in alkalies, but readily soluble in hydrochloric, nitric, and acetic acids.

The separation of the precipitate is materially promoted by addition of ammonium chloride. From very dilute solutions the precipitate separates only after standing some time in a warm place. Ammonium oxalate, tartrate,

* Mn is bivalent in the manganous compounds: Mn is quadrivalent or Mn_2 is sexivalent in the manganic oxides and salts: in the manganates and permanganates (?) Mn is also a hexad.

† If the quantity of the precipitate is only trifling, the color appears yellowish white.

and especially citrate retard the precipitation, the latter salt also keeps up some of the manganese. In the presence of ammonia and ammonium sulphide in large excess, the flesh-colored hydrated precipitate occasionally passes into the green anhydrous sulphide even in the cold, the change being greatly facilitated by boiling, and being hindered more or less by the presence of ammonium chloride. Solutions containing much free ammonia must first be nearly neutralized with hydrochloric acid.

6. *Potassa, soda,* and *ammonia* produce whitish precipitates of MANGANOUS HYDROXIDE ($Mn(OH)_2$), which upon exposure to the air speedily acquire a brownish and finally a deep blackish-brown color, owing to the conversion of the manganous hydroxide into manganic hydroxide by the absorption of oxygen from the air.

Ammonia and ammonium carbonate do not redissolve this precipitate; but presence of ammonium chloride prevents the precipitation by ammonia altogether, and that by potassa partly. Of already formed precipitates solution of ammonium chloride redissolves only those parts which have not yet undergone oxidation. The solution of the manganous hydroxide in ammonium chloride is owing to the disposition of the manganous salts to form double salts with ammonium salts. The ammoniacal solutions of these double salts turn brown in the air, and deposit dark-brown manganic hydroxide.

N. B. Non-volatile organic acids impede the precipitation of manganese by alkali carbonates. Sugar impedes the precipitation by alkalies, but not that by alkali carbonates.

7. *Potassium ferrocyanide* throws down MANGANESE FERROCYANIDE ($Mn_2 Fe Cy_6$) as a reddish-white precipitate, soluble in hydrochloric acid.

8. *Potassium ferricyanide* precipitates brown MANGANESE FERRICYANIDE ($Mn_3 Fe_2 Cy_{12}$) insoluble in hydrochloric acid and ammonia.

9. If a few drops of a fluid containing manganous salt, and free from chlorine, are sprinkled on *lead dioxide,* and nitric acid free from chlorine is added, the mixture boiled and allowed to settle, the fluid acquires a red color, from the formation of permanganic acid, $H Mn O_4$ (HOPPE-SEYLER).

10. *Barium carbonate* does not precipitate aqueous solutions of manganous salts upon digestion in the cold, with the exception of manganous sulphate.

11. If any compound of manganese, in a state of minute division, is fused with 2 or 3 parts of *sodium carbonate* on a platinum wire, or on a small strip of platinum foil (heated by directing the flame upon the lower surface), in the *outer* flame of the Bunsen lamp or blowpipe, SODIUM MANGANATE ($Na_2 Mn O_4$) is formed, which makes the fused mass appear GREEN while hot, and of a BLUISH-GREEN tint after cooling, the bead at the same time losing its transparency. This reaction enables us to detect the smallest traces of manganese.

12. *Borax* and *sodium metaphosphate* dissolve manganese compounds in the outer gas or blowpipe flame to clear VIOLET-RED beads, which upon cooling acquire an AMETHYST-RED tint; they lose their color in the inner flame, owing to a reduction of manganic borate or phosphate to manganous salts. The borax bead appears black when containing a considerable portion of manganic borate, but that formed by sodium metaphosphate never loses its transparency. The latter loses its color in the inner flame of the blowpipe far more readily than the former.

§ 108.

c. NICKEL, Ni. 58.8.*

1. METALLIC NICKEL in the fused state is yellowish white, inclining to gray; it is bright, hard, malleable, difficultly fusible; it does not oxidize in the air at the common temperature, but it oxidizes slowly upon ignition; it is attracted by the magnet and may itself become magnetic. It slowly dissolves in hydrochloric acid and dilute sulphuric acid upon the application of heat, with evolution of hydrogen gas. It dissolves readily in nitric acid. The solutions contain nickelous salts.

2. NICKELOUS HYDROXIDE is light green, and remains unaltered in the air, but is converted by ignition into amorphous green NICKELOUS OXIDE (Ni O). Both nickelous oxide and the corresponding hydroxide are readily soluble in hydrochloric, nitric and sulphuric acids. But the nickelous oxide which crystallizes in octahedrons is insoluble in acids; it dissolves, however, in fusing sodium disulphate. NICKELIC OXIDE ($Ni_2 O_3$) is black; it dissolves in hydrochloric acid to nickelous chloride with evolution of chlorine. By gentle ignition of the nitrate, nickelous oxide containing a little nickelic oxide of grayish-green color is obtained.

3. Most of the NICKEL SALTS are yellow in the anhydrous, green in the hydrated state; their solutions are light green. The soluble normal salts slightly redden litmus paper, and are decomposed at a red heat.

4. *Hydrogen sulphide* does not precipitate solutions of nickel salts with strong acids in presence of free acids; in the absence of free acids a small portion of the nickel gradually separates as black NICKEL SULPHIDE (Ni S).

Nickel acetate is not precipitated, or scarcely at all, in presence of free acetic acid. But in the absence of free acid the greater part of the nickel is thrown down by long-continued action of hydrogen sulphide.

5. *Ammonium sulphide* produces in neutral, and hydrogen sulphide in alkaline solutions, a black precipitate of NICKEL

* In the monoxide and all the salts Ni is bivalent, in the sesquioxide Ni_2 is sexivalent.

SULPHIDE (Ni S), which is not altogether insoluble in ammonium sulphide, especially if the latter contain free ammonia; the fluid from which the precipitate has been thrown down exhibits therefore usually a brownish color, which is discharged on prolonged boiling, with complete separation of the nickel sulphide. The presence of ammonium chloride, and still more of ammonium acetate, considerably promotes the precipitation. Nickel sulphide dissolves scarcely at all in acetic acid, with great difficulty in hydrochloric acid, but readily in nitro-hydrochloric acid upon application of heat.

6. *Potassa* and *soda* produce a light green precipitate of NICKELOUS HYDROXIDE ($Ni(OH)_2$), which is insoluble in an excess of the precipitants, and unalterable in the air, and on boiling (even in the presence of alcohol). Ammonium carbonate dissolves this precipitate, when filtered and washed, to a greenish-blue fluid, from which potassa or soda reprecipitates the nickel as apple-green hydroxide.

7. *Ammonia* added in small quantity produces a trifling greenish turbidity; upon further addition of the reagent this redissolves readily to a blue fluid containing a compound of NICKELOUS SALT AND AMMONIA. Potassa and soda precipitate from this solution nickelous hydroxide. Solutions containing ammonium salts or free acid are not rendered turbid by ammonia.

N.B. The presence of non-volatile organic acids, and of sugar, impedes the precipitation by alkalies.

8. *Potassium ferrocyanide* precipitates greenish-white FERROCYANIDE OF NICKEL, $Ni_2Fe(CN)_6$, which is insoluble in hydrochloric acid.

9. *Potassium ferricyanide* precipitates yellowish-brown NICKEL FERRICYANIDE ($Ni_3CO_3(CN)_{12}$), which is insoluble in hydrochloric acid.

10. *Potassium cyanide* produces a yellowish-green precipitate of NICKEL CYANIDE ($Ni(CN)_2$), which redissolves readily in an excess of the precipitant as a double nickel potassium cyanide ($Ni(CN)_2 . 2KCN$); the solution is brownish-yellow, and does not acquire a darker color on exposure to the air. If sulphuric acid or hydrochloric acid is added to this solution, the potassium cyanide is decomposed, and the nickel cyanide reprecipitated. From more highly dilute solutions the nickel cyanide separates only after some time; it is very difficultly soluble in an excess of the precipitating acids in the cold, but more readily upon boiling. If the solution of the double cyanide is rendered alkaline by solution of soda, being also kept so by a further addition of soda if necessary, and chlorine gas is passed into it without warming, the whole of the nickel gradually separates as black nickelic hydroxide ($Ni(OH)_3$).

11. On adding to solutions which are not too dilute and which have been

rendered alkaline by ammonia, a solution of potassium sulphocarbonate,* a deep brownish-red fluid is obtained which is barely translucent, and appears almost black by reflected light. If the solution of nickel is extremely dilute, the addition of the reagent will produce a delicate pink color (C. D. BRAUN). The occurrence of this color in highly dilute solutions is characteristic of nickel.

12. *Barium carbonate*, on digestion in the cold, does not precipitate solutions of nickel salts, solution of sulphate alone excepted.

13. *Potassium nitrite* with acetic acid does not throw down nickel, even from concentrated solutions. In the presence of calcium, barium or strontium, however, a yellow crystalline double nitrite of nickel and of the alkali-earth metal is precipitated from not too dilute solutions. The precipitate is difficultly soluble in cold water, more readily in hot water to a green fluid (KÜNZEL, O. L. ERDMANN).

14. *Borax* and *sodium metaphosphate* dissolve compounds of nickel in the outer flame to clear beads. The borax bead is violet while hot, reddish-brown when cold; the sodium metaphosphate bead is reddish or brownish-red while hot, yellow or reddish-yellow when cold. In the inner flame the sodium metaphosphate bead remains unaltered, but the borax bead becomes gray and cloudy from reduced metal. On continued heating the particles of nickel collect together without fusing, and the bead loses its color.

15. By the reduction in the *stick of charcoal*, according to p. 31, the compounds of nickel yield after trituration white, shining, ductile spangles, which will be deposited on the point of a magnetic knife in the form of a brush. With nitric acid they give a green solution, which can be further examined.

§ 109.

d. COBALT, Co. 58.8.†

1. METALLIC COBALT in the fused state is steel-gray, pretty hard, malleable, difficultly fusible, and magnetic; susceptible of polish; it does not oxidize in

* Prepared by taking a solution containing about 5 per cent. of K O H, saturating one-half with H_2S, adding the other half and then $\frac{1}{25}$ of the volume of CS_2, digesting at a gentle heat, and finally separating the dark orange-red fluid from the undissolved CS_2. The solution must be kept in a well-closed bottle.

† In the cobaltous compounds, Co is bivalent; in the cobaltic salts Co is quadrivalent and Co_2 sexivalent. The cobaltic salts, save the double cyanides, nitrides and amides, are unstable.

the air at the common temperature, but it oxidizes at a red heat; with acids it behaves like nickel. The solutions contain cobaltous salts.

2. COBALTOUS OXIDE (Co O) is light brown; cobaltous hydroxide is a pale red powder. Both dissolve readily in hydrochloric, nitric, and sulphuric acids. COBALTIC OXIDE, ($Co_2 O_3$) is black; it dissolves in cold hydrochloric acid to cobaltic chloride ($Co_2 Cl_6$), but on heating this is converted into cobaltous chloride ($Co Cl_2$), with evolution of chlorine.

3. The COBALTOUS SALTS containing water of crystallization are red, the anhydrous salts mostly blue. The moderately concentrated solutions appear of a light red color, which they retain though considerably diluted. The soluble normal salts redden litmus slightly, and are decomposed at a red heat; cobaltous sulphate alone can bear a moderate red heat without suffering decomposition. When a solution of cobaltous chloride is evaporated, the light red color changes toward the end of the operation to blue; addition of water restores the red color.

4. *Hydrogen sulphide* does not precipitate solutions of salts with strong acids, if they contain free acid; from neutral solutions it gradually precipitates part of the cobalt as black cobaltous sulphide (Co S).

Cobaltous acetate is not precipitated, or to a very slight extent, in presence of free acetic acid. But in the absence of free acid it is completely precipitated, or almost completely.

5. *Ammonium sulphide* precipitates from neutral, and hydrogen sulphide from alkaline solutions, the whole of the metal as black COBALTOUS SULPHIDE (Co S). Ammonium chloride promotes the precipitation most materially. Cobaltous sulphide is insoluble in alkalies and ammonium sulphide, scarcely soluble in acetic acid, very difficultly soluble in hydrochloric acid, upon application of heat.

6. *Potassa* and *soda* produce blue precipitates of BASIC COBALTOUS SALTS, insoluble in excess of the precipitants, which turn green upon exposure to the air, owing to the absorption of oxygen.

Upon boiling they are converted into pale red COBALTOUS HYDROXIDE, which contains alkali, and generally appears rather discolored from cobaltic hydroxide formed in the process. If, before boiling, alcohol is added, the precipitate is rapidly converted into dark brown cobaltic hydroxide. Normal ammonium carbonate dissolves the washed precipitates of cobaltous basic salt or cobaltous hydroxide completely to intensely violet-red fluids, in which a somewhat larger proportion of potassa or soda produces a blue precipitate, the fluid still retaining its violet colors.

7. *Ammonia* produces the same precipitate as potassa, but this redissolves in an excess of the ammonia to a reddish

fluid, which turns brownish-red on exposure to the air, from which potassa or soda throws down a portion of the cobalt as blue basic salt. Ammonia produces no precipitate in solutions containing ammonium salts or a free acid.

N.B. The presence of non-volatile organic acids or sugar checks the precipitation by alkalies.

8. *Potassium ferrocyanide* throws down green COBALTOUS FERROCYANIDE $Co_2 F_2 (CN)_6$, insoluble in hydrochloric acid.

9. *Potassium ferricyanide* throws down brownish-red COBALTOUS FERRICYANIDE, $Co_3 Fe_2 (CN)_{12}$, insoluble in hydrochloric acid.

10. Addition of *potassium cyanide* gives rise to the formation of a brownish-white precipitate of COBALTOUS CYANIDE, $Co(CN)_2$, which dissolves readily in excess of the precipitant as a double cobaltous potassium cyanide, $Co(CN)_2 . 4(K C N)$. Acids precipitate from the solution cobaltous cyanide. But if the solution is boiled with potassium cyanide in excess, in presence of free hydrocyanic acid (liberated by addition of one or two drops of hydrochloric acid), or if the solution is mixed with potassa or soda and chlorine is passed through it without warming, the double cyanide is converted into potassium cobalticyanide, $K_6 Co_2 (CN)_{12}$, and acids will now produce no precipitate (essential difference between cobalt and nickel). Potassium nitrite, and acetic acid added to the unaltered solution of the double cyanide produce a blood-red color in consequence of the formation of cobalt potassium nitrocyanide; when the liquid is very dilute the color is merely orange-red. Solution of soda added to the double cyanide occasions a brown color when the fluid is shaken, oxygen being absorbed (essential differences between cobalt and nickel, C. D. BRAUN).

11. *Potassium sulphocarbonate*, added to solutions which have been rendered alkaline by ammonia, produces a dark brown, almost black color; if the solution is very dilute a pale straw color.

12. Addition of tartaric or citric acid, then of ammonia in excess, and lastly of *potassium ferricyanide*, produces a deep yellowish-red color; with extremely dilute solutions a rose color (SKEY). This is a very delicate reaction, well suited for the detection of cobalt in the presence of nickel.

13. *Barium carbonate* behaves in the same way as to solutions of nickel.

14. If *potassium nitrite* is added in not too small proportion to the solution of a cobaltous salt, then acetic acid to strongly acid reaction, and the mixture put in a moderately warm place, all the cobalt separates, from concentrated solutions very soon, from dilute solutions after some time, in the form of a crystalline precipitate of a beautiful yellow color (FISCHER, STROMEYER). This precipitate is TRIPOTASSIUM COBALTIC NITRITE, $(K N O_2)_6 . Co_2(N O_2)_6 + Aq_x$ (SADTLER). The precipitate is very perceptibly soluble in water, scarcely soluble in concentrated solutions of potassium salts and in alcohol, insoluble in presence of potassium nitrite. When boiled with water it

dissolves, though not copiously, to a red fluid, which remains clear upon cooling, and from which alkalies throw down cobaltous hydroxide. This reaction serves well to distinguish and separate cobalt from nickel.

15. *Borax* dissolves compounds of cobalt in the inner and outer flame to clear beads of a magnificent blue color, which appear violet by candlelight, and are almost black in the presence of a large quantity of cobalt. This test is as delicate as it is characteristic. *Sodium metaphosphate* gives the same reaction, but it is less delicate.

16. In the reduction with the *stick of charcoal*, according to p. 31, compounds of cobalt behave in the same way as compounds of nickel. The solution with nitric acid is red.

§ 110.

e. Iron and Ferrous Compounds,* Fe. 56.

1. Metallic iron in the pure state has a light whitish-gray color (iron containing carbon is more or less gray); the metal is hard, lustrous, malleable, ductile, exceedingly difficult to fuse, and is attracted by the magnet. In contact with air and moisture a coating of rust (ferric hydroxide) forms on its surface: upon ignition in the air a coating of black ferrous-ferric oxide Fe_3O_4. Hydrochloric and dilute sulphuric acids dissolve iron, with evolution of hydrogen; if the iron contains carbide, the hydrogen is mixed with hydrocarbons. The solutions contain ferrous salts. Dilute nitric acid dissolves iron in the cold to ferrous nitrate, with evolution of nitrogen monoxide; at a high temperature to ferric nitrate, with evolution of nitrosyl (p. 270); if the iron contains carbide, some carbon dioxide is also evolved, and there is left undissolved a brown substance resembling humus, which is soluble in alkalies; when graphite is present, it also is left behind.

2. Ferrous oxide is black; ferrous hydroxide is white, and in the moist state absorbs oxygen and speedily acquires a grayish-green, and ultimately a brownish-red color. Both ferrous oxide and ferrous hydroxide are readily dissolved by hydrochloric, sulphuric, and nitric acids.

3. The ferrous salts have in the anhydrous state a white, in the hydrated state a greenish color; their solutions only look greenish when concentrated. The latter absorb oxygen when exposed to the air, with precipitation of basic ferric salts. Chlorine or nitric acid converts them by boiling into ferric salts. The soluble normal salts redden litmus-paper, and are decomposed at a red heat.

4. Solutions of ferrous salts made acid by strong acids are not precipitated by *hydrogen sulphide;* nor are neutral solu-

* Fe is bivalent in the ferrous compounds. Fe is quadrivalent and Fe_2 is sexivalent in the ferric salts.

tions nor solutions acidified with weak acids precipitated by this reagent, or at the most but very incompletely.

5. *Ammonium sulphide* precipitates from neutral, and hydrogen sulphide from alkaline solutions, the whole of the metal as black FERROUS SULPHIDE (Fe S), which is insoluble in alkalies and sulphides of the alkali metals, but dissolves readily in hydrochloric and nitric acids; this black precipitate turns reddish brown in the air by oxidation. To highly dilute solutions ammonium sulphide imparts a green color, and it is only after some time that the ferrous sulphide separates as a black precipitate. Ammonium chloride promotes the precipitation most materially.

6. *Potassa* and *ammonia* produce a precipitate of FERROUS HYDROXIDE, $Fe(OH)_2$, which in the first moment looks almost white, but acquires after a very short time a dirty green, and ultimately a reddish-brown color, owing to absorption of oxygen from the air. Presence of ammonium salts prevents the precipitation by potassa partly, and that by ammonia altogether.

If alkaline ferrous solutions thus obtained by the agency of ammonium salts are exposed to the air, ferrous-ferric and ferric hydroxides precipitate. Non-volatile organic acids, sugar, etc., check the precipitation by alkalies.

7. *Potassium ferrocyanide* produces a bluish-white precipitate of POTASSIUM FERROUS FERROCYANIDE, $K_2Fe_2(CN)_6$, which by absorption of oxygen from the air, speedily acquires a blue color. Nitric acid or chlorine converts it immediately into Prussian blue, $6\,K_2Fe_2(CN)_6 + Cl_6 = Fe_7(CN)_{18} + 3K_4Fe(CN)_6 + Fe_2Cl_6$.

8. *Potassium ferricyanide* produces a magnificently blue precipitate of FERROUS FERRICYANIDE, Fe_5Cy_{12}. This precipitate does not differ in color from Prussian blue. It is insoluble in hydrochloric acid, but is readily decomposed by potassa. In highly dilute solutions the reagent produces simply a deep blue-green coloration.

9. *Potassium sulphocyanate* does not alter solutions of ferrous salts when free from ferric salts.

10. *Barium carbonate* does not precipitate solutions of ferrous salts in the cold, with the exception of the sulphate.

11. *Borax* dissolves ferrous compounds in the oxidizing flame, giving beads varying in color from yellow to a dark

red; when cold the beads vary from colorless to dark yellow. In the inner flame the beads change to bottle-green, owing to the reduction of the newly formed ferric borate to ferrous-ferric borate. *Sodium metaphosphate* shows a similar reaction; the beads produced with this reagent lose their color upon cooling still more completely than those produced with borax; the signs of the ensuing reduction in the reducing flame are also less marked.

12. When reduced in the *stick of charcoal* (p. 31), ferrous compounds give a dull black powder, which is attracted by a magnetic knife. The reduced metal, when dissolved in a few drops of aqua regia, gives a yellow fluid, which can be further tested according to § 111.

§ 111.

f. Iron in Ferric Compounds, Fe. 56.

1. Native crystallized FERRIC OXIDE (Fe_2O_3) is steel-gray; the native as well as the artificially prepared ferric oxide gives upon trituration a brownish-red powder; the color of the ferric hydroxides is more inclined to reddish-brown. Both ferric oxide and the ferric hydroxides dissolve in hydrochloric, nitric and sulphuric acids; the normal ferric hydroxide, $Fe(OH)_3$, dissolves readily in these acids, but the basic ferric hydroxides, and ferric oxide dissolve with greater difficulty, and completely only after long and hot digestion. FERROUS-FERRIC OXIDE (Fe_3O_4) is black; it dissolves in hydrochloric acid to ferrous chloride and ferric chloride, in aqua regia to ferric chloride.

2. The normal anhydrous FERRIC SALTS are nearly white; the basic salts are yellow or reddish-brown. The color of the solutions is brownish-yellow, and becomes reddish-yellow upon the application of heat. The soluble normal salts redden litmus paper, and are decomposed by heat.

3. *Hydrogen sulphide* produces in solutions made acid by stronger acids a milky white turbidity, proceeding from separated SULPHUR; the ferric salt being at the same time converted into ferrous salt: $Fe_2(SO_4)_3 + H_2S = 2\,FeSO_4 + H_2SO_4 + S$.

If solution of hydrogen sulphide is rapidly added to neutral solutions, a transient blackening of the fluid also occurs. From solution of normal ferric acetate, hydrogen sulphide throws down the greater part of the iron; but in presence of a sufficient quantity of free acetic acid sulphur alone separates.

4. *Ammonium sulphide* precipitates from neutral, and hydrogen sulphide from alkaline solutions, the whole of the

metal as black FERROUS SULPHIDE (Fe S) mixed with sulphur; $Fe_2 Cl_6 + 3 (NH_4)_2 S = 6 NH_4 Cl + 2 Fe S + S$.

In very dilute solutions the reagent produces only a blackish-green coloration. The minutely divided ferrous sulphide subsides in such cases only after long standing. Ammonium chloride most materially promotes the precipitation. Ferrous sulphide, as already stated (§ 110, 5), is insoluble in alkalies and alkali sulphides, but dissolves readily in hydrochloric and nitric acids.

5. *Potassa* and *ammonia* produce bulky reddish-brown precipitates of NORMAL FERRIC HYDROXIDE ($Fe (OH)_3$), which are insoluble in an excess of the precipitant as well as in ammonium salts.

Non-volatile organic acids and sugar, when present in sufficient quantity, entirely prevent the precipitation.

6. *Potassium ferrocyanide* produces, even in highly dilute solutions, a magnificently blue precipitate of FERRIC FERROCYANIDE, or Prussian blue, $Fe_7 Cy_{18}$:—$3 K_4 Fe Cy_6 + 2 Fe_2 Cl_6 = 12 K Cl + Fe_7 Cy_{18}$. This precipitate is insoluble in hydrochloric acid, but is decomposed by potassa, with separation of ferric hydroxide.

7. *Potassium ferricyanide* deepens the color of solutions of ferric salts to reddish-brown; but it fails to produce a precipitate.

8. *Potassium sulphocyanate* imparts to acid solutions a most intense blood-red color, arising from the formation of a soluble FERRIC SULPHOCYANATE.

This color does not disappear on the addition of a little alcohol and warming (difference from the analogous reaction of nitrosyl (NO), § 158). Solutions of ferric salts, containing sodium acetate (which consequently are more or less red from ferric acetate), do not show the blood-red color of the sulphocyanate till after the addition of much hydrochloric acid. The same remark applies to solutions containing an alkali fluoride, phosphate or borate, or an oxalate, tartrate, racemate, malate, citrate, or succinate. This test will indicate the presence of iron even in fluids, which are so highly dilute that every other reagent fails to produce in them the slightest visible alteration. The red coloration may in such cases be detected most distinctly by resting the test-tube upon a sheet of white paper, and looking through it from the top. The delicacy of the reaction may also be increased by shaking gently with ether after the addition of hydrochloric acid, and of excess of potassium sulphocyanate solution freshly prepared from the crystals. The ferric sulphocyanate dissolves in the ether, and the layer of the latter acquires a more or less red color.

9. *Barium carbonate* precipitates even in the cold all the iron as FERRIC HYDROXIDE MIXED WITH A BASIC SALT.

10. When a solution containing a ferric salt is rendered nearly neutral by sodium carbonate, and then heated to boiling with addition of excess of *sodium acetate*, all the iron is precipitated as brown BASIC FERRIC ACETATE, and may be completely removed from the solution by filtering hot and washing with boiling water. If it is allowed to remain in the solution it may partially redissolve as the latter becomes cold.

11. The reactions before the *blowpipe* are the same as with the ferrous compounds.

§ 112.

Recapitulation and remarks.—On observing the reactions of the several metals of the fourth group with solution of potassa, it would appear that the separation of zinc, whose hydroxide is soluble in an excess of this reagent, might be readily effected by its means; but in the actual experiment we find that notable quantities of zinc are thrown down with ferric hydroxide, cobaltous hydroxide, etc., to such an extent, indeed, that it is often impossible tc demonstrate the presence of zinc in the alkaline filtrate. This method would be entirely inadmissible in the presence of chromic oxide, as solutions of the latter and of zinc oxide in potassa mutually precipitate each other.

Again, the reactions of the different metals with ammonium chloride and an excess of ammonia would lead to the conclusion that the separation of iron as ferric hydroxide from cobalt, nickel, manganese and zinc might be readily effected by these agents. But this method also is inaccurate, since greater or smaller portions of the other metals will always precipitate along with the ferric hydroxide; and it may therefore happen that small quantities of cobalt, manganese, etc., altogether escape detection in this process.

It is far safer therefore to separate the other metals of the fourth group from ferric hydroxide by barium carbonate, as in that case the IRON is precipitated free from zinc and manganese, and, if ammonium chloride is added previously to the addition of the barium carbonate, almost entirely free also from nickel and cobalt. Instead of using the barium carbonate for the separation of ferric hydroxide, we may proceed as follows: Nearly neutralize any excess of acid with sodium carbonate, add sodium acetate and boil; or mix the sufficiently diluted solution with a rather large quantity of ammonium chloride, cautiously add ammonium carbonate till the fluid commences to become cloudy, the reaction still remaining acid, and then boil. In each of these last two methods the basic ferric salt must be filtered off hot.

Manganese may be separated from cobalt and nickel, as well as from zinc, by treating the washed precipitated sulphides with moderately dilute acetic acid, which dissolves the manganese sulphide, leaving the other sulphides undissolved. If the acetic solution is now evaporated and mixed with solution of potassa, the least trace of a precipitate will be sufficient to recognize the MANGANESE before the blowpipe with sodium carbonate. If the sulphides left undissolved by acetic acid are now treated, after washing, with very dilute hy-

drochloric acid, zinc sulphide dissolves, leaving almost the whole of the cobalt and nickel sulphides behind. If the fluid is then boiled, and strongly concentrated to expel the hydrogen sulphide, and afterwards treated with solution of potassa or soda in excess without warming, the ZINC is sure to be detected in the filtrate by passing into it hydrogen sulphide.

In practical analysis we generally separate the whole of the metals of the fourth group as sulphides by precipitation with ammonium sulphide in presence of ammonium chloride. It is convenient to separate nickel and cobalt, or at least the far larger portion of these two metals, at the outset. To this end the moist precipitate of the sulphides is treated with water and some hydrochloric acid, with active stirring, but without application of heat. Nearly the whole of the nickel sulphide and cobalt sulphide is left behind undissolved, whilst all the other sulphides are dissolved, being converted into chlorides. The undissolved residue of cobalt sulphide and nickel sulphide is filtered and washed. A portion is tested with borax in the inner blowpipe flame; COBALT may generally be thus detected with certainty even in the presence of nickel. The detection of nickel in presence of cobalt is not quite so simple a matter. It is best done by warming the rest of the residue with a little aqua regia, diluting, filtering, evaporating the solution to remove all free acid, adding a little water and a sufficiency of potassium nitrite, acidifying with acetic acid, and setting aside in a moderately warm place for at least twelve hours. The cobalt then separates as tripotassium cobaltic nitrite; the NICKEL may be precipitated from the filtrate by solution of soda, and tested before the blowpipe, or according to § 108, 11, after considerable dilution.

For the detection of small quantities of nickel in presence of large quantities of cobalt, it is still better to use the solution of the cyanides in potassium cyanide mixed with solution of soda. In this solution the presence of cobalt will be shown by a dark color on exposure to the air, the presence of nickel by the separation of black nickelic hydroxide on treatment with chlorine (§ 108, 10, and § 109, 10).

By boiling the filtrate from the sulphides of nickel and cobalt with nitric acid, the iron passes from the state of ferrous chloride, as it existed in the solution of the sulphide, into that of ferric chloride. After the free acid has been nearly neutralized by sodium carbonate, the iron may be thrown down as basic ferric salt by barium carbonate in the cold. Manganese

and zinc remain in the filtrate; these metals are then also precipitated with ammonium sulphide and some ammonium chloride, the precipitate is filtered and washed, and treated with hydrochloric acid (which may leave small quantities of cobalt and nickel sulphides undissolved). The solution of zinc and manganese chlorides is evaporated nearly to dryness to remove free acid, mixed with excess of sodium hydroxide, which precipitates both zinc and manganese as hydroxides, but redissolves the former. Dilute and filter. Test the precipitate for MANGANESE by fusion before the blowpipe with sodium carbonate, and the filtrate for ZINC by means of hydrogen sulphide.

The trifling quantities of cobalt and nickel, dissolved on the first treatment of the sulphide precipitate with dilute hydrochloric acid, remain with the zinc sulphide in the separation of the latter from the manganese sulphide by acetic acid—or with the manganous hydroxide if the separation is effected by solution of potassa or soda. The zinc sulphide may be extracted from the blackish precipitate by dilute hydrochloric acid, and the detection of the manganese in presence of the cobalt and nickel may be readily effected by means of sodium carbonate in the outer flame.

In the presence of non-volatile organic bodies the whole of the metals must be precipitated as sulphides, since such organic substances would check the precipitation of ferric hydroxide by barium carbonate.

Ferrous and ferric salts may be detected in presence of each other by testing for the former with potassium ferricyanide, for the latter with potassium ferrocyanide or sulphocyanate.

Special Reactions of the rarer Metals of the Fourth Group.

§ 113.

a. URANIUM, U. 240.

This metal is found in a few minerals, as pitchblende, uran-ochre, etc. Uranium forms two oxides, viz., uranous oxide (UO_2), and uranic oxide (UO_3). Uranous oxide is brown; it dissolves in nitric acid to uranic nitrate. The uranic hydroxide is yellow; at about 300° it loses its water and turns red; it is converted by ignition into the dark blackish-green uranous-uranic oxide (U_3O_8). The solutions of uranic oxide in acids are yellow. *Hydrogen sulphide* does not alter them; *ammonium sulphide* throws down from them, after neutralization of the free acid, a slowly subsiding precipitate, which is readily soluble in acids, even acetic acid. The precipitation is promoted by ammonium chloride. The precipitate, when formed in the cold, is chocolate brown, and contains uranic oxysulphide, ammonium sulphide, and water. It

is insoluble in yellow ammonium sulphide ; but, when free from other sulphides, it dissolves to a notable extent in colorless ammonium sulphide, forming a black fluid. On being washed, the precipitate is gradually converted into yellow uranic hydroxide. On warming or boiling the mixture of uranium solution and ammonium sulphide, the oxysulphide at first thrown down splits into sulphur and black uranous oxide, which last is insoluble in the excess of ammonium sulphide (REMELÉ). The uranic oxysulphide (but not the precipitate which has been converted into uranous oxide and sulphur) dissolves readily in ammonium carbonate. (This reaction may be used as a means of separating uranium from zinc, manganese, iron, etc.) If the oxysulphide remains long in contact with the fluid which has turned black in consequence of partial solution of the precipitate in excess of ammonium sulphide, it gradually turns blood-red, probably from becoming crystalline (REMELÉ). *Ammonia, potassa,* and *soda* produce yellow precipitates containing uranic hydroxide and alkali, which are insoluble in excess of the precipitants. *Ammonium carbonate* and *hydrogen potassium carbonate* produce yellow precipitates of ammonium or potassium uranic carbonate, which *readily redissolve in an excess of the precipitants.* Potassa and soda throw down from such solutions the whole of the uranium. *Barium carbonate* completely precipitates solutions of uranic salts, even in the cold (essential difference from nickel, cobalt, manganese, and zinc, and means of separating uranium from these metals). *Potassium ferrocyanide* produces a reddish-brown precipitate (a most delicate test). *Borax* and *sodium metaphosphate* give with uranium compounds in the inner flame of the blowpipe green beads, in the outer flame yellow beads, which acquire a yellowish-green tint on cooling.

b. THALLIUM, Tl. 204.

Thallium occurs, in minute quantities, in many kinds of copper and iron pyrites, in many kinds of crude sulphur, and accumulates in the flue-dust of the lead chambers, where the furnaces are fed with thalliferous pyrites. It is occasionally found in commercial sulphuric and hydrochloric acids, and it has been discovered in lepidolite, preparations of cadmium and bismuth, in ores of zinc, mercury, and antimony, in the ashes of plants, and in some saline waters. Thallium is a metal resembling lead, of 11.86 spec. grav., soft, fuses at 290°, volatile at a white heat, and in a current of hydrogen at a red heat, crackling like tin when bent ; it does not decompose water, even on addition of acid. Dilute sulphuric and nitric acids readily dissolve it ; hydrochloric acid dissolves it with difficulty. It forms two oxides. THALLIOUS OXIDE (Tl_2O), is black, and fusible; when in the melted state it attacks glass or porcelain. It dissolves in water to hydroxide ; the solution is colorless, alkaline, caustic, and absorbs carbonic acid. From the solution THALLIOUS HYDROXIDE (Tl O H) may be obtained in yellow crystals, which dissolve in alcohol. THALLIC OXIDE (Tl_2O_3) is insoluble in water and dark violet, THALLIC HYDROXIDE (Tl O.O H) is brown. Thallic oxide is hardly acted on by concentrated sulphuric acid in the cold, on heating they combine. On continued heating oxygen escapes and thallious sulphate is formed. Treated with hydrochloric acid, thallic oxide yields the corresponding chloride, as a white crystalline mass, which splits into chlorine and thallious chloride when heated. In solutions of THALLIC SALTS alkalies throw down thallic hydroxide, hydrogen sul-

phide produces thallious salts with separation of sulphur, potassium iodide yields thallious iodide and iodine, hydrochloric acid produces no change. The THALLIOUS SALTS are colorless, some are readily soluble in water (sulphate, nitrate, phosphate, tartrate, acetate), some are difficultly soluble (carbonate, chloride), some are almost insoluble (iodide, etc.). On boiling solutions of thallious salts with nitric acid they are not converted into thallic salts, but they are so converted entirely by boiling and evaporating with aqua regia. *Potassa*, *soda*, and *ammonia* do not precipitate aqueous solutions of thallious salts, *carbonated alkalies* throw down thallious carbonate, but only from very concentrated solutions (for 100 parts of water dissolve 5.23 parts at 18°). *Hydrochloric acid* throws down thallious chloride, if the solutions are not extremely dilute, in the form of a white readily subsiding precipitate, unalterable in the air, still less soluble in dilute hydrochloric acid than in water. *Potassium iodide* precipitates, even from the most dilute solutions, the light yellow thallious iodide, which is almost insoluble in water, but somewhat more soluble in solution of potassium iodide. *Platinic chloride* precipitates from solutions which are not extremely dilute the pale orange thallious platinic chloride ($2\ Tl\ Cl . Pt\ Cl_4$), which is very difficultly soluble. *Hydrogen sulphide* does not precipitate solutions rendered strongly acid by mineral acids, unless arsenious acid is present, when a brownish-red precipitate is formed, which contains the whole of the arsenic and a part of the thallium. Neutral or very slightly acid solutions are incompletely precipitated by this reagent; from acetic acid solutions the whole of the thallium is thrown down as black thallious sulphide. *Ammonium sulphide* precipitates the whole of the thallium as black sulphide, which readily collects into lumps, especially on warming; hydrogen sulphide added to alkaline solutions has the same effect. The sulphide thrown down is insoluble in ammonia, alkali sulphides and potassium cyanide, it rapidly oxidizes in the air to thallious sulphate, it dissolves readily in dilute hydrochloric, sulphuric, and nitric acids, but it is acted on only with difficulty by acetic acid. On heating it first fuses and then volatilizes. *Zinc* throws down the metal in the form of black crystalline laminæ. *Colorless flames* are tinged intensely green by compounds of thallium. The *spectrum* of thallium exhibits only one line (compare the spectrum plate) of an emerald green color, extremely characteristic. If the quantity of metal is small, the line soon disappears. The spectroscope generally affords the best means of detecting thallium. Thalliferous pyrites often give the green line at once. To look for thallium in crude sulphur, it is best to remove the greater part of the sulphur with carbon disulphide, and then to test the residue. In the presence of much sodium with very small quantities of thallium the green line will not be seen, unless you moisten the substance and examine the spectrum which is first produced. For the detection of thallium in the wet way, potassium iodide is the most delicate reagent; if a ferric salt is present, it must previously be reduced by sodium sulphite.

c. INDIUM, In. 113.4

Indium has hitherto been discovered only in the blende of Freiburg, in the zinc prepared from the same, and in wolfram. It is a white, highly lustrous metal, and resembles platinum in color, it is very soft, ductile, makes a mark on paper, is capable of receiving a polish, and preserves its lustre in the air

and in water even when boiling. It fuses about as easily as lead. On charcoal before the blowpipe it melts with a shining metallic surface, colors the flame blue, and yields an incrustation which is dark yellow while hot, light yellow when cold, and cannot be easily dispersed by the blowpipe flame. Indium dissolves in dilute hydrochloric and sulphuric acids with evolution of hydrogen, slowly in the cold, more rapidly on heating; in concentrated sulphuric acid it dissolves with evolution of sulphur dioxide; in nitric acid it dissolves with ease even when the acid is cold and dilute. The oxide, In_2O_3, is brown when hot, straw-colored when cold, it does not color vitreous fluxes; when ignited in hydrogen or with charcoal, it is readily reduced, and if a flux be used metallic globules will be obtained. The ignited oxide dissolves slowly in acids in the cold, but readily and completely by the aid of heat. The salts are colorless, the sulphate, nitrate and chloride dissolve readily in water. The chloride is volatile and hygroscopic. *Alkalies* throw down the hydroxide in the form of a white bulky precipitate, which is completely insoluble in potassa and ammonia; tartaric acid prevents the precipitation. *Alkali carbonates* precipitate a white gelatinous carbonate. When recently thrown down the precipitate dissolves in ammonium carbonate, but not in potassium or sodium carbonate; if the solution in ammonium carbonate is boiled, the indium carbonate separates again. *Sodium phosphate* throws down a white bulky precipitate. *Alkali oxalates* produce a crystalline precipitate. *Sodium acetate* added to the nearly neutral solution of the sulphate throws down on boiling a basic sulphate. *Barium carbonate* precipitates the whole of the indium, on digestion in the cold, in the form of basic salt. (Means of separating indium from zinc, manganese, cobalt, nickel, and ferrous compounds.) *Hydrogen sulphide* produces no precipitate in the presence of a strong acid. From dilute and slightly acid solutions it throws down some of the indium, as in the case of zinc. From a solution acidified with acetic acid this reagent throws down indium sulphide in the form of a slimy precipitate of a fine yellow color. *Ammonium sulphide* added to a solution mixed with tartaric acid and ammonia produces a white precipitate, which probably consists of indium hydrosulphide, and which turns yellow on treatment with acetic acid. Indium sulphide is insoluble in cold, but soluble in hot ammonium sulphide; on cooling it separates from the solution with a white color. *Potassium ferrocyanide* produces a white precipitate. *Potassium ferricyanide, sulphocyanate* and *chromate* produce no precipitate. *Zinc* precipitates the metal in the form of white shining laminæ. Indium compounds produce a peculiar bluish violet tinge in a *colorless flame*. The *spectrum* has a characteristic intensely blue line (at 111–112° of the scale; see the spectrum plate), and a fainter violet line which appears brightest with the chloride, but they are very transient. For obtaining more persistent lines the sulphide is the most suitable compound.

d. Vanadium, V. 51.2.

Vanadium occurs in the form of vanadates, occasionally in small quantities in iron and copper ores, and in the slags obtained from the same. There are five oxides of vanadium, the monoxide V_2O, the dioxide V_2O_2, the trioxide V_2O_3, the tetroxide V_2O_4, and the pentoxide V_2O_5: Roscoe. V_2O_2 is gray, possesses metallic lustre, is insoluble in water, and is soluble in dilute acids, with evolution of hydrogen, to blue fluids which bleach organic coloring mat-

ters by reducing them. V_2O_3 is black, insoluble, not reduced by ignition in hydrogen; exposed to the air it is gradually converted into V_2O_4. Acid solutions containing V_2O_3 are green. V_2O_4 is dark blue, acid solutions in which it is present are pure blue. All the lower oxides pass into V_2O_5 on heating with nitric acid or aqua regia, on fusing with potassium nitrate, or on igniting in oxygen or air. V_2O_5 is non-volatile, fusible, solidifies to a crystalline mass, dark red to orange-red in color. Heated to redness in a current of hydrogen it is converted to V_2O_3. V_2O_5 is difficultly soluble in water, but the solution reddens litmus-paper strongly. It dissolves in acids and combines with bases yielding vanadates. *a. Acid solutions.*—The stronger acids dissolve V_2O_5 to red or yellow fluids, which are frequently decolorized by boiling. The sulphuric acid solution when much diluted, treated with *zinc* and warmed gently, turns first blue, then green, and finally from lavender to violet. The V_2O_5 is thus reduced to V_2O_2, and on addition of ammonia a brown hydroxide is precipitated, which immediately absorbs oxygen. *Sulphur dioxide, hydrogen sulphide,* and *organic substances* reduce the solutions, but only to V_2O_4, hence the color produced is only blue. *Ammonium sulphide* produces a brown color, and on acidifying with hydrochloric acid, or better with sulphuric acid, the brown pentasulphide falls, which is soluble in excess of ammonium sulphide with a brownish-red color. *Potassium ferrocyanide* throws down a green flocculent precipitate which is insoluble in acids. *Tincture of galls* produces after some time in solutions free from excess of acid a brownish-black precipitate. *b. Vanadates.*—V_2O_5 yields five series of vanadates, viz., tribasic, bibasic, monobasic, biacid and triacid. The monobasic salts (metavanadates) are mostly yellow, those of the alkali metals are colorless. Some of them pass by warming with water into colorless isomeric salts. The acid vanadates are yellow or yellowish-red. The vanadates sustain a red heat, most of them are soluble in water, all are soluble in nitric acid. The alkali vanadates are soluble in water in inverse proportion to the quantity of free alkali or alkali salt present. When mixed with *acids,* the solutions acquire a yellow or red color; *silver nitrate, mercurous nitrate, barium chloride* and *lead acetate* produce white or yellow precipitates readily soluble in acids; *ammonium sulphide* reacts as in acid solutions, *potassium ferrocyanide* produces a yellow precipitate, *tincture of galls* produces a deep black color, especially in solutions of acid vanadates of alkali metals. If the solution of an alkali vanadate is saturated with *ammonium chloride,* the whole of the vanadic acid separates as white ammonium metavanadate, insoluble in solution of ammonium chloride (most characteristic reaction). The precipitate gives by ignition V_2O_5 or a mixture of the same with a lower oxide. If an acidified solution of alkali vanadates is shaken with *hydrogen dioxide* the fluid acquires a red tint; if ether is then added, and the mixture shaken, the solution retains its color, the ether remaining colorless (most delicate reaction). WERTHER. *Borax* dissolves vanadium compounds in the inner and outer flame to a clear bead; the bead produced in the outer flame is colorless, with large quantities of vanadium yellow; the bead produced in the inner flame has a beautiful green color; with larger quantities of vanadium it looks brownish whilst hot, and only turns green on cooling.

§ 114.

FIFTH GROUP.

More common metals:—SILVER, MERCURY, LEAD, BISMUTH, COPPER, CADMIUM.

Rarer metals:—PALLADIUM, RHODIUM, OSMIUM, RUTHENIUM.

Properties of the group.—The sulphides are insoluble both in dilute acids and in alkali sulphides.* The solutions of these metals are therefore completely precipitated by hydrogen sulphide, no matter whether they be neutral, or contain free acid or free alkali. The fact that the solutions of the metals of the fifth group are precipitated by hydrogen sulphide in presence of a free strong acid, distinguishes them from the metals of the fourth group and generally from the metals of all the preceding groups.

For the sake of greater clearness and simplicity, we divide the more common metals of this group into two classes, and distinguish:

1. METALS PRECIPITABLE BY HYDROCHLORIC ACID, viz., silver, mercury in mercurous salts, lead.

2. METALS NOT PRECIPITABLE BY HYDROCHLORIC ACID, viz., mercury in mercuric salts, copper, bismuth, cadmium.

Lead must be considered in both classes, since the sparing solubility of its chloride might lead to confounding it with silver and mercury in mercurous salts, without affording us on the other hand any means of effecting its perfect separation from the metals of the second division.

Special Reactions of the more common Metals of the Fifth Group.

FIRST DIVISION; METALS WHICH ARE PRECIPITATED BY HYDROCHLORIC ACID.

§ 115.

a. SILVER,† Ag. 108.

1. METALLIC SILVER is white, very lustrous, moderately hard, highly malleable, rather difficultly fusible. It is not oxidized by fusion in the air.

* Consult, however, the paragraphs on copper and mercury, as the latter remark applies only partially to them.

† In the ordinary or argentic compounds Ag is univalent. The nature of the argentous compounds is not sufficiently understood, but Ag_2 appears to be univalent in them.

Nitric acid dissolves silver readily; the metal is insoluble in dilute sulphuric acid and in hydrochloric acid.

2. ARGENTIC OXIDE, Ag_2O, is a grayish-brown powder; it is not altogether insoluble in water, and dissolves readily in dilute nitric acid. There is no corresponding hydroxide. Ag_2O is decomposed by heat into metallic silver and oxygen gas. The black argentous oxide Ag_4O and SILVER DIOXIDE Ag_2O_2 are likewise decomposed by heat into metallic silver and oxygen.

3. The ARGENTIC SALTS are non-volatile and colorless; many of them acquire a black tint upon exposure to light. The soluble normal salts do not alter vegetable colors, and are decomposed at a red heat.

4. *Hydrogen sulphide* and *ammonium sulphide* precipitate black SILVER SULPHIDE (Ag_2S), which is insoluble in dilute acids, alkalies, alkali sulphides, and potassium cyanide. Boiling nitric acid decomposes and dissolves this precipitate readily, with separation of sulphur.

5. *Potassa* and *soda* precipitate ARGENTIC OXIDE in the form of a grayish-brown powder, which is insoluble in an excess of the precipitants, but dissolves readily in ammonia.

6. *Ammonia*, if added in very small quantity to neutral solutions, throws down ARGENTIC OXIDE as a brown precipitate, which readily redissolves in an excess of ammonia. Acid solutions are not precipitated.

7. *Hydrochloric acid* and *soluble metallic chlorides* produce a white curdy precipitate of ARGENTIC CHLORIDE (Ag Cl). In very dilute solutions these reagents impart at first simply a bluish-white opalescent appearance to the fluid; but after long standing in a warm place the silver chloride collects at the bottom of the vessel. By the action of light the white silver chloride loses chlorine, first acquiring a violet tint, and ultimately turning black (probably from formation of argentous chloride Ag_4Cl_2); it is insoluble in nitric acid, but dissolves readily in ammonia as ammonio-silver chloride ($2\,AgCl.3\,NH_3$), from which double compound the silver chloride is again separated by acids.

Concentrated hydrochloric acid and concentrated solutions of chlorides of the alkali metals dissolve silver chloride to a very perceptible amount, more particularly upon application of heat; but the dissolved chloride separates again upon dilution. Upon exposure to heat silver chloride fuses without decomposition, giving upon cooling a translucent horny mass.

8. If compounds of silver mixed with *sodium carbonate* are exposed on a charcoal support to the *inner flame of the blowpipe*, white brilliant malleable metallic globules are obtained, with or without a slight dark red incrustation of the charcoal.

The metal is also readily reduced in the *stick of charcoal* (p. 31).

§ 116.

b. MERCURY,* Hg. 200; AND MERCUROUS COMPOUNDS.

1. METALLIC MERCURY is grayish-white, lustrous, fluid at the common temperature; it solidifies at —39°, and boils at 360°. It is insoluble in hydrochloric acid; in dilute cold nitric acid it dissolves to mercurous nitrate, in concentrated hot nitric acid to mercuric nitrate.

2. MERCUROUS OXIDE, Hg_2O, is a black powder, readily soluble in nitric acid. It is decomposed by the action of heat, the mercury volatilizing in the metallic state. There is no corresponding hydroxide.

3. The MERCUROUS SALTS volatilize upon ignition; most of them suffer decomposition in this process. Mercurous chloride and mercurous bromide volatilize unaltered. Most of the mercurous salts are colorless. The soluble normal salts redden litmus paper. Mercurous nitrate is decomposed by addition of much water into a light yellow insoluble basic and soluble acid salt.

4. *Hydrogen sulphide* and *ammonium sulphide* produce a black precipitate which is insoluble in dilute acids, ammonium sulphide, and potassium cyanide. The precipitate, especially after warming, consists of MERCURIC SULPHIDE MIXED WITH MERCURY. Sodium monosulphide, in presence of some caustic soda, dissolves this precipitate with separation of metallic mercury; sodium disulphide dissolves it without separation of metallic mercury; the solutions contain mercuric sulphide. The precipitate gives up mercury to boiling concentrated nitric acid with formation of a white double mercuric compound, namely. $2\,Hg\,S.Hg\,(N\,O_3)_2$. The precipitate is readily dissolved by aqua regia.

5. *Potassa*, *soda*, and *ammonia* produce black precipitates which are insoluble in an excess of the precipitants. The precipitates produced by the fixed alkalies consist of MERCUROUS OXIDE; whilst those produced by ammonia consist of MERCUROSAMMONIUM SALTS.

6. *Hydrochloric acid* and *soluble metallic chlorides* precipitate MERCUROUS CHLORIDE (Hg_2Cl_2) as a fine powder of dazzling whiteness. Cold hydrochloric acid and cold nitric acid fail to dissolve this precipitate; it dissolves, however, although very difficultly and slowly, upon long-continued boiling with these acids, being resolved by hydrochloric acid into mercuric chloride and metallic mercury, which separates; and converted by nitric acid into mercuric chloride and mercuric nitrate. Nitro-hydrochloric acid and chlorine water dissolve

* In mercurous compounds Hg_2 is bivalent, *e.g.*, $\begin{matrix} Hg \\ | \\ Hg \end{matrix}\!\!>\!O$ and $\begin{matrix} Hg\text{–}Cl \\ | \\ Hg\text{–}Cl \end{matrix}$

In mercuric salts Hg is bivalent, *e.g.*, $Hg<^{Cl}_{Cl}$ and $Hg{=}O$.

the mercurous chloride readily, converting it into mercuric chloride. Ammonia and potassa decompose mercurous chloride, separating from it, the former dimercurosammonium chloride, $N H_2Hg_2Cl$, the latter mercurous oxide.

7. If a drop of a neutral or slightly acid solution is put on a *clean and smooth surface of copper*, and washed off after some time, the spot will afterwards, on being gently rubbed with cloth, paper, etc., appear white and lustrous like silver. The application of a gentle heat to the copper causes the metallic mercury precipitated on its surface to volatilize, and thus removes the apparent silvering.

8. *Stannous chloride* produces a gray precipitate of METALLIC MERCURY, which may be united into globules by boiling the metallic deposit, after decanting the fluid, with hydrochloric acid, to which a little stannous chloride may also be added.

9. If an intimate mixture of an anhydrous compound of mercury with anhydrous *sodium carbonate* is introduced into a sealed glass tube, and covered with a layer of sodium carbonate, and the tube is then strongly heated, the mercurial compound invariably undergoes decomposition, and METALLIC MERCURY separates, forming a coat of gray sublimate above the heated part of the tube. By means of a lens the sublimate will be seen to consist of globules of metal. Larger globules may be obtained by rubbing the sublimate with a glass rod.

§ 117.

c. LEAD, Pb. 207.

1. METALLIC LEAD is bluish-gray ; its surface recently cut exhibits a metallic lustre ; it is soft, malleable, readily fusible ; it evaporates at a white heat. Fused upon charcoal before the blowpipe it forms a coating of yellow oxide on the support. Hydrochloric acid and moderately concentrated sulphuric acid act upon it but little, even with the aid of heat ; but dilute nitric acid dissolves it readily, more particularly on heating.

2. LEAD MONOXIDE Pb O is a yellow or reddish-yellow powder, looking brownish-red whilst hot, and fusible at a red heat. Lead hydroxide $Pb(OH)_2$ is white. Both the oxide and hydroxide dissolve readily in nitric and acetic acids. LEAD SUBOXIDE (Pb_2O) is black, MINIUM ($2Pb O . Pb O_2$) is red, the so-called SESQUIOXIDE is light brown, the DIOXIDE is brown. They are all of them converted into the monoxide by ignition in the air. The dioxide is not dissolved by heating with nitric acid, but it dissolves readily in that menstruum on addition of some alcohol. The solution contains lead nitrate $Pb(NO_3)_2$.

3. The LEAD SALTS are non-volatile ; most of them are colorless ; the

normal soluble salts redden litmus paper, and are decomposed at a red heat. If lead chloride is ignited in the air, part of it volatilizes, and leaves behind a mixture of lead oxide and lead chloride. In the lead salts Pb is bivalent.

4. *Hydrogen sulphide* and *ammonium sulphide* produce black precipitates of LEAD SULPHIDE (Pb S), which are insoluble in *cold* dilute acids, in alkalies and alkali sulphides, and cyanides. Lead sulphide is decomposed by hot nitric acid. If the acid was dilute, the whole of the lead is obtained in solution as lead nitrate, and sulphur separates; if the acid was fuming, the sulphur is also completely oxidized, and insoluble lead sulphate alone is obtained; if the acid was of medium concentration, both processes take place, a portion of the lead being obtained in solution as nitrate, whilst the remainder separates as sulphate, together with the unoxidized sulphur. In solutions of lead salts containing a large excess of a concentrated mineral acid, hydrogen sulphide produces a precipitate only after the addition of water or after partial neutralization of the free acid by an alkali. If a lead solution is precipitated by hydrogen sulphide in presence of a large quantity of free hydrochloric acid, a red precipitate is occasionally formed, consisting of lead chloro-sulphide, which is however converted by an excess of hydrogen sulphide into black lead sulphide.

5. *Potassa, soda,* and *ammonia* throw down HYDROXIDE MIXED WITH BASIC SALTS in the form of white precipitates, which are insoluble in ammonia, but soluble in potassa and soda. In solutions of lead acetate ammonia (free from carbonate) does not immediately produce a precipitate, owing to the formation of a soluble lead di- or triacetate.

6. *Sodium carbonate* throws down a white precipitate of BASIC LEAD CARBONATE, *e.g.*, $2PbCO_3.Pb(OH)_2$, which is not quite insoluble in a large excess of the precipitant, especially on heating, but is insoluble in potassium cyanide.

7. *Hydrochloric acid* and *soluble chlorides* produce in concentrated solutions heavy white precipitates of LEAD CHLORIDE ($PbCl_2$), which are soluble in a large amount of water, especially upon application of heat. Lead chloride is converted by ammonia into lead oxychloride, $PbCl_2.3PbO$, which is also a white powder, but almost absolutely insoluble in water. In dilute nitric and hydrochloric acids lead chloride is more difficultly soluble than in water.

8. *Sulphuric acid* and *sulphates* produce white precipitates of

LEAD SULPHATE ($PbSO_4$), which are nearly insoluble in water and dilute acids. From dilute solutions, especially from such as contain much free acid, the lead sulphate precipitates only after some time, frequently only after a long time. It is advisable to add a considerable excess of dilute sulphuric acid, as this tends to increase the delicacy of the reaction, lead sulphate being more insoluble in dilute sulphuric acid than water. The separation of small quantities of lead sulphate is best effected by evaporating, after the addition of the sulphuric acid, as far as practicable on the water-bath, and then treating the residue with water, or, if allowable, with alcohol. Lead sulphate is slightly soluble in concentrated nitric acid; it dissolves with difficulty in boiling concentrated hydrochloric acid, but more readily in solution of potassa. It dissolves also pretty readily in the solutions of some ammonium salts, particularly in solution of ammonium acetate; dilute sulphuric acid precipitates it again from these solutions.

9. *Potassium chromate* produces a yellow precipitate of LEAD CHROMATE ($PbCrO_4$), which is readily soluble in potassa, but difficultly so in dilute nitric acid.

10. If a mixture of a compound of lead with *sodium carbonate* is exposed on a charcoal support to the *reducing flame of the blowpipe*, soft malleable METALLIC GLOBULES OF LEAD are readily produced, the charcoal becoming covered at the same time with a yellow incrustation of LEAD OXIDE. The reduction may be also readily effected by means of the stick of charcoal.

11. The *metallic incrustation*, obtained according to p. 33, is black with brown edge, the *incrustration of oxide* is light yellow ochre, the *incrustation of iodide* varies from the yellow of the lemon to that of the yolk of an egg, the *incrustation of sulphide* varies from brownish-red to black, and is not dissolved by ammonium sulphide (BUNSEN).

§ 118.

Recapitulation and remarks.—The metals of the first division of the fifth group are most distinctly characterized in their chlorides; since the different reactions of these chlorides with water and ammonia afford us a simple means both of

detecting them and of effecting their separation from one another. For if the precipitate containing the three metallic chlorides is boiled with a somewhat large quantity of water, or boiling water is repeatedly poured over it on the filter, the lead chloride dissolves, whilst the silver chloride and the mercurous chloride remain undissolved. If these two chlorides are then treated with ammonia, the mercurous chloride is converted into the black dimercurosammonium salt, insoluble in an excess of ammonia, described in § 116, 6, whilst the silver chloride dissolves readily in ammonia, and precipitates from this solution again upon addition of nitric acid. (When operating upon small quantities it is advisable first to expel the greater part of the ammonia by heat.) In the aqueous solution of lead chloride the metal may be readily detected by sulphuric acid.

SECOND DIVISION: METALS WHICH ARE NOT PRECIPITATED BY HYDROCHLORIC ACID.

§ 119.

a. Mercury in Mercuric Compounds.

1. Mercuric Oxide (Hg O) is generally crystalline, and has a bright red color, which upon reduction to powder changes to a dull yellowish red ; the oxide precipitated from solutions of mercuric nitrate or chloride forms a yellow powder. It is not quite insoluble in water, it turns gray in the air. Upon exposure to heat it transiently acquires a deeper tint ; at a dull red heat it is resolved into metallic mercury and oxygen. Both the crystalline and non-crystalline oxide dissolve readily in hydrochloric acid and in nitric acid.

2. The mercuric salts volatilize upon ignition ; they suffer decomposition in this process ; mercuric chloride, bromide, and iodide volatilize unaltered. On boiling a solution of the chloride, some of the salt escapes with the steam. Most of the mercuric salts are colorless. The soluble normal salts redden litmus paper. The nitrate and sulphate are decomposed by a large quantity of water into soluble acid and insoluble basic salts.

3. Addition of a very small quantity of *hydrogen sulphide* or *ammonium sulphide* produces, after shaking, a perfectly white precipitate. Addition of somewhat larger quantity of these reagents causes the precipitate to acquire a yellow, orange, or brownish-red color; an excess of the precipitant produces a black precipitate of mercuric sulphide (Hg S). This progressive variation of color from white to black,

which depends on the proportion of the hydrogen sulphide or ammonium sulphide added, distinguishes the mercuric salts from all other bodies. The white precipitate which forms at first consists of a double compound of mercuric sulphide with the still undecomposed portion of the mercuric salt (in a solution of mercuric chloride, for instance, $Hg\,Cl_2 . 2\,Hg\,S$); the gradually increasing admixture of black sulphide causes the precipitate to pass through the several gradations of color above mentioned. Ammonium sulphide only dissolves the smallest traces of mercuric sulphide; the least amount of mercury is dissolved when the precipitate is digested hot with yellow ammonium sulphide. Potassa and potassium cyanide do not dissolve mercuric sulphide, and it is entirely insoluble in hydrochloric and in nitric acid, even on boiling. By the very protracted action of hot concentrated nitric acid the precipitate is converted into a white body, consisting of $2\,Hg\,S . Hg\,(N\,O_3)_2$. Potassium sulphide and sodium sulphide in the presence of potash or soda dissolve the precipitate completely, but it is insoluble in potassium hydrosulphide, and in sodium hydrosulphide. Aqua regia decomposes the precipitate and dissolves it with ease. In mercuric solutions containing a large excess of concentrated mineral acid, hydrogen sulphide produces a precipitate only after the addition of water.

4. *Potassa* added in small quantity produces in neutral or slightly acid solutions a reddish-brown precipitate, which acquires a yellow tint if the reagent is added in excess. The reddish-brown precipitate is a BASIC SALT; the yellow precipitate consists of MERCURIC OXIDE ($Hg\,O$). An excess of the precipitant does not redissolve these precipitates. In very acid solutions this reaction does not take place at all, or at least the precipitation is very incomplete. In presence of ammonium salts potassa produces white precipitates. The precipitate thrown down by potassa from a solution of mercuric chloride containing an excess of ammonium chloride is of analogous composition to the precipitate produced by ammonia (see 5).

5. *Ammonia* produces white precipitates quite analogous to those produced by potassa in presence of ammonium chloride; thus, for instance, ammonia precipitates from solutions of mercuric chloride a MERCURAMMONIUM CHLORIDE ($N\,H_2Hg\,Cl$).

6. *Stannous chloride* added in small quantity to solution of mercuric chloride, or to solutions of mercuric salts in presence of hydrochloric acid, throws down MERCUROUS CHLORIDE ($2\,Hg\,Cl_2 + Sn\,Cl_2 = Hg_2\,Cl_2 + Sn\,Cl_4$). By addition of a

larger quantity of the reagent the precipitated mercurous chloride is reduced to METAL ($Hg_2Cl_2 + SnCl_2 = Hg_2 + SnCl_4$). The precipitate, which was white at first, acquires therefore now a gray tint, and may, after it has subsided, be readily united into globules of metallic mercury by boiling with hydrochloric acid and a little stannous chloride.

7. If a little *galvanic element*, made out of a slip of platinum foil and a slip of tin foil, joined at one end with a wooden clamp, but otherwise apart from each other, is introduced into a mercuric solution acidified with hydrochloric acid, all the mercury will gradually be precipitated by preference upon the platinum. On removing the foils, drying and heating strongly in a glass tube, globules of mercury will be obtained, which may be more distinctly seen under the microscope. On heating this mercury with a fragment of iodine, it will be converted into red mercuric iodide (VAN DEN BROEK).

8. Mercuric salts show the same reaction as mercurous salts with metallic *copper* and when heated with *sodium carbonate* in a glass tube.

§ 120.

b. COPPER,* Cu. 63.4.

1. METALLIC COPPER has a peculiar red color, and a strong lustre; it is moderately hard, malleable, rather difficultly fusible; in contact with water and air it becomes covered with a green crust of basic cupric carbonate; upon ignition in the air it becomes coated over with cuprous oxide and cupric oxide. In hydrochloric acid and dilute sulphuric acid it is insoluble or nearly so, even upon boiling. Nitric acid dissolves the metal readily. Concentrated sulphuric acid converts it into cupric sulphate, with evolution of sulphur dioxide.

2. CUPROUS OXIDE (Cu_2O) is red, CUPROUS HYDROXIDE ($Cu_2(OH)_2$) is yellow; both change to cupric oxide upon ignition in the air. On treating cuprous oxide with dilute sulphuric acid metallic copper separates, whilst cupric sulphate dissolves; on treating cuprous oxide with hydrochloric acid white cuprous chloride is formed, which dissolves in an excess of the acid, but is reprecipitated from this solution by water.

3. CUPRIC OXIDE is a black powder; CUPRIC HYDROXIDE ($Cu(OH)_2$), is of a light blue color. Both dissolve readily in hydrochloric, sulphuric, and nitric acids.

4. Most of the normal CUPRIC SALTS are soluble in water; the soluble salts redden litmus, and suffer decomposition when heated to gentle redness, with the exception of the sulphate, which can bear a somewhat higher temperature. They are usually white in the anhydrous state; the hydrated salts are usually of a blue or green color, which their solutions continue to exhibit even when much diluted.

5. *Hydrogen sulphide* and *ammonium sulphide* produce in

* In the cuprous compounds Cu_2, in the cupric salts Cu is bivalent.

alkaline, neutral, and acid solutions brownish-black precipitates of CUPRIC SULPHIDE, Cu S. This sulphide is insoluble in dilute acids and caustic alkalies. Hot solutions of potassium sulphide and sodium sulphide fail also to dissolve it or dissolve it only to a very trifling extent; but it is a little more soluble in ammonium sulphide. [Yellow ammonium sulphide produces in the cold a red-brown or red precipitate, $Cu_2(NH_4)_2S_7$, which dissolves completely in an excess of the reagent, but is almost perfectly precipitated as black sulphide when the solution is heated to boiling.] Cupric sulphide is readily decomposed and dissolved by boiling nitric acid, but it remains altogether unaffected by boiling dilute sulphuric acid. It dissolves completely in solution of potassium cyanide. In solutions of cupric salts which contain a very large excess of a concentrated mineral acid, hydrogen sulphide produces a precipitate only after the addition of water.

6. *Potassa* or *soda* produces a light blue bulky precipitate of CUPRIC HYDROXIDE ($Cu(OH)_2$). If the solution is highly concentrated, and the precipitant is added in excess, the precipitate turns black after the lapse of some time, and loses its bulkiness, even in the cold, from conversion into cupric oxide, but the change takes place immediately if the precipitate is boiled with the fluid in which it is suspended. $Cu(OH)_2 = CuO + H_2O$.

7. *Sodium carbonate* produces a greenish-blue precipitate of BASIC CUPRIC CARBONATE ($CuCO_3.Cu(OH)_2$), which upon boiling changes to cupric oxide, and dissolves in ammonia to an azure-blue, and in potassium cyanide to a colorless fluid.

8. *Ammonia* added in small quantity to solutions of normal cupric salts produces a greenish-blue precipitate, consisting of a BASIC CUPRIC SALT. This precipitate redissolves readily, upon further addition of ammonia, to a perfectly clear fluid of a magnificent azure-blue, which owes its color to the formation of a CUPRODIAMMONIUM SALT. Thus, for instance, in a solution of cupric sulphate excess of ammonia produces $(N_2H_6Cu)SO_4$. In solutions containing a certain amount of free acid, ammonia produces no precipitate, but this azure-blue coloration makes its appearance the instant the ammonia predominates. The blue color ceases to be perceptible only in very dilute solutions.

Potassa produces in such blue solutions in the cold, after the lapse of some time, a precipitate of blue cupric hydroxide; but upon boiling the fluid this

reagent precipitates the whole of the copper as black cupric oxide. Ammonium carbonate shows the same reaction as ammonia.

N.B. In the presence of non-volatile organic acids the cupric salts are not precipitated by caustic or carbonated alkalies, the resulting solutions having a deep blue color. In presence of sugar or similar organic substances caustic alkalies produce precipitates which are soluble in excess of the precipitants; sodium carbonate, however, produces a permanent precipitate.

9. *Potassium ferrocyanide* produces in moderately dilute solutions a reddish-brown precipitate of cupric FERROCYANIDE, $Cu_2 Fe (CN)_6$, insoluble in dilute acids, but decomposed by potassa. In very highly dilute solutions the reagent merely produces a reddish coloration.

10. If the solution of a cupric salt is mixed with sulphurous acid or with hydrochloric acid and sodium sulphite, and *potassium sulphocyanate* is then added, CUPROUS SULPHOCYANATE $Cu_2 (CNS)_2$ is thrown down. The precipitate is white, and is practically insoluble in water and dilute acids.

11. *Metallic iron* when brought into contact with concentrated solutions of salts of copper is almost immediately covered with a coating of METALLIC COPPER; very dilute solutions produce this coating only after some time. Presence of a little free acid accelerates the reaction. If a fluid containing copper and a little free hydrochloric acid is poured into a *platinum capsule* (the lid of the platinum crucible), and a small piece of *zinc* is introduced, the bright platinum surface speedily becomes covered with a COATING OF COPPER; even with very dilute solutions this coating is clearly discernible. If a piece of iron wire is inserted into a spiral formed from a rather stout *platinum wire*, and the whole is then placed in a slightly acidified solution of copper, the platinum wire will after some time be found to be coated with COPPER.

12. If a mixture of a compound of copper with *sodium carbonate* is exposed on a charcoal support to the *inner flame of the blowpipe*, METALLIC COPPER is obtained, without incrustation of the charcoal. The reduction may be also very conveniently effected in the stick of charcoal (p. 31). The best method of freeing the copper from the particles of charcoal is to triturate the fused mass in a small mortar with water, and to cautiously wash off the charcoal powder, when the copper-red metallic particles will be left behind.

13. If copper, or some alloy containing copper, or a trace of a salt of copper, or even simply the loop of a platinum wire dipped in a highly dilute copper

solution, is introduced into the fusing zone of the *gas flame*, or exposed to the inner *blowpipe flame*, the upper or outer portion of the flame shows a magnificent emerald-green tint. Addition of hydrochloric acid to the sample considerably heightens the beauty and delicacy of this reaction. The flame then has an azure color.

14. *Borax* readily dissolves oxides of copper in the outer gas or blowpipe flame. The beads are green while hot, blue when cold. In the inner flame the bead is colorless unless a very large quantity of copper is present; when cold it is red and opaque. In the lower reducing flame of the Bunsen gas flame the bead does not become red-brown until the addition of stannic oxide, when this change rapidly takes place, owing to the production of cuprous oxide. If the bead is introduced alternately into the lower oxidizing zone and the lower reducing zone, it becomes ruby red and transparent.

§ 121.

c. BISMUTH,* Bi. 210.

1. BISMUTH has a reddish tin-white color and moderate metallic lustre; it is of medium hardness, brittle, readily fusible; fused upon a charcoal support it forms an incrustation of yellow trioxide, Bi_2O_3. It dissolves readily in nitric acid, but is nearly insoluble in hydrochloric acid and altogether so in dilute sulphuric acid. Concentrated sulphuric acid converts it into bismuth sulphate with evolution of sulphur dioxide.

2. BISMUTH TRIOXIDE (bismuthous oxide) is a yellow powder, which transiently acquires a deeper tint when heated. It fuses at a red heat. Bismuth hydroxide, Bi O OH, is white. Both the trioxide and hydroxide dissolve readily in hydrochloric, sulphuric and nitric acids, yielding the bismuth salts. The grayish-black DIOXIDE, Bi_2O_2, and the red PENTOXIDE, Bi_2O_5, are converted into trioxide by ignition in the air. By heating with nitric acid they are converted into bismuth nitrate.

3. Most of the BISMUTH SALTS are non-volatile and are decomposed at a red heat. Bismuth trichloride is volatile. The bismuth salts are colorless or white; some of them are soluble in water, others insoluble. The soluble salts redden litmus paper; they are decomposed by a large quantity of water into insoluble basic salts, which separate, whilst the greater portion of the acid remains in solution together with some bismuth.

4. *Hydrogen sulphide* and *ammonium sulphide* produce in bismuth solutions black precipitates of BISMUTH TRISULPHIDE, Bi_2S_3, which is insoluble in dilute acids, alkalies, alkali sul-

* In all its common compounds bismuth is trivalent: in some it is apparently bivalent, but in fact trivalent, *e.g.*, Bi_2Cl_4; or, $\begin{matrix} Bi{-}Cl_2 \\ | \\ Bi{-}Cl_2 \end{matrix}$. In bismuth pentoxide it is quinquivalent.

phides, and potassium cyanide, but is readily decomposed and dissolved by boiling nitric acid. In solutions of salts of bismuth which contain a very considerable excess of hydrochloric or nitric acid, hydrogen sulphide produces a precipitate only after the addition of water.

5. *Potassa* and *ammonia* throw down BISMUTH HYDROXIDE, Bi O O H, as a white precipitate, which is insoluble in an excess of the precipitant.

6. *Sodium carbonate* and *ammonium carbonate* throw down BASIC BISMUTH CARBONATE ($Bi_2 O_2 C O_3$) as a white bulky precipitate, which is insoluble in excess of the precipitant, and in potassium cyanide. Warming assists the precipitation.

7. *Potassium dichromate* precipitates BISMUTH CHROMATE, $Bi_2 (Cr O_4)_3$, as a yellow powder. This substance differs from lead chromate in being readily soluble in dilute nitric acid and insoluble in potassa.

8. *Dilute sulphuric acid* fails to precipitate moderately dilute solutions of bismuth nitrate. On evaporating with an excess of sulphuric acid on the water-bath to dryness, a white saline mass of bismuth trisulphate $Bi_2 (S O_4)_3$ * is left, which always dissolves readily to a clear fluid in water acidified with sulphuric acid (characteristic difference between bismuth and lead). After long standing (several days occasionally) bismuth disulphate, $Bi (Bi O) 2 S O_4 + 3 H_2 O$,† separates from this solution in white microscopic needle-shaped crystals, which dissolve in nitric acid.

9. The reaction which characterizes bismuth more particularly is the decomposition of its normal or triacid salts by *water*, which is attended with separation of insoluble basic salts. The addition of a large amount of water to solutions of bismuth salts causes the immediate formation of a dazzling white precipitate, provided there be not too much free acid present. If the basic or disulphate above mentioned (8), be treated with much water, it is converted into the more basic monosulphate $(Bi O)_2 S O_4 + H_2 O$.‡ This reaction is the most sensitive with bismuth trichloride, as the BASIC BISMUTH CHLORIDE or oxychloride, Bi O Cl is almost absolutely insoluble in water. Where water fails to precipitate nitric acid

* $Bi{-}SO_4$, $>SO_4$, $Bi{-}SO_4$ † $Bi{-}SO_4$, $>O$, $Bi{-}SO_4$ ‡ $Bi{-}O$, $>SO_4$, $Bi{-}O$

solutions of bismuth, owing to the presence of too much free acid, a precipitate will almost invariably make its appearance immediately upon addition of solution of sodium chloride or ammonium chloride. Presence of tartaric acid does not interfere with the precipitation of bismuth by water.

10. On mixing a solution of bismuth with an excess of solution of *stannous chloride in potassa or soda*, a black precipitate of bismuth dioxide will fall. This is a very characteristic and delicate reaction.

11. If a mixture of a compound of bismuth with *sodium carbonate* is exposed on a charcoal support to the *reducing flame*, brittle GLOBULES OF BISMUTH are obtained, which fly into pieces under the stroke of a hammer. The charcoal becomes covered at the same time with a slight incrustation of BISMUTH TRIOXIDE, which is orange-colored whilst hot, yellow when cold. The reduction may be also conveniently effected in the stick of charcoal (p. 31). On triturating the end of the charcoal stick containing the reduced metal, yellowish spangles will be obtained.

12. Bismuth compounds, even in minute quantities, when heated on charcoal in the blowpipe flame, with a mixture of equal parts of *sulphur* and *potassium iodide*, yield a very volatile intensely scarlet sublimate of BISMUTH IODIDE (V. KOBELL).

13. The *metallic incrustation*, obtained according to p. 33, is black with a brown edge. The *incrustation of oxide* is yellowish white; it is turned black by stannous chloride and soda, see 10 (difference from the lead incrustation). The *incrustation of iodide* is bluish-brown with red edge. The *incrustation of sulphide* is umber-colored with coffee-colored edge, not dissolved by ammonium sulphide (BUNSEN).

§ 122.

d. CADMIUM, Cd. 112.

1. METALLIC CADMIUM has a tin-white color; it is lustrous, not very hard, malleable; it fuses at a temperature below red heat, and volatilizes at a temperature somewhat above the boiling point of mercury, and may therefore easily be sublimed in a glass tube. Heated on charcoal before the blowpipe it takes fire and burns, emitting brown fumes of cadmium oxide, which form a coating on the charcoal. Hydrochloric acid and dilute sulphuric acid dissolve it, with evolution of hydrogen, but nitric acid dissolves it most readily.

2. CADMIUM OXIDE, Cd O, is a brown, fixed powder; its HYDROXIDE,

$Cd(OH)_2$, is white. Both dissolve readily in hydrochloric, nitric, and sulphuric acids.

3. The CADMIUM SALTS are colorless or white; some of them are soluble in water. The soluble normal salts redden litmus paper, and are decomposed at a red heat.

4. *Hydrogen sulphide* and *ammonium sulphide* produce in alkaline, neutral, and acid solutions, bright yellow precipitates of CADMIUM SULPHIDE (Cd S), which are insoluble in dilute acids, alkalies, alkali sulphides, and potassium cyanide (difference from copper). They are readily decomposed and dissolved by boiling nitric acid, as well as by boiling hydrochloric acid and by boiling dilute sulphuric acid (difference from copper). In solutions of cadmium containing a large excess of acid, hydrogen sulphide produces a precipitate only after dilution with water.

5. *Potassa* and *soda* produce white precipitates of CADMIUM HYDROXIDE, $Cd(OH)_2$; which are insoluble in an excess of the precipitants.

6. *Ammonia* likewise precipitates white CADMIUM HYDROXIDE, which, however, redissolves readily and completely to a colorless fluid in an excess of the precipitant.

7. *Sodium carbonate* and *ammonium carbonate* produce white precipitates of CADMIUM CARBONATE ($Cd C O_3$), which are insoluble in an excess of the precipitants. The presence of ammonium salts impedes the precipitation; free ammonia prevents it. The precipitate is readily soluble in potassium cyanide. It takes some time to separate from dilute solutions; warming assists the separation greatly.

8. *Potassium sulphocyanate* does not throw down solutions of cadmium, even after the addition of sulphurous acid (difference from copper).

9. If a mixture of a compound of cadmium with *sodium carbonate* is exposed on a charcoal support to the *reducing flame*, the charcoal becomes covered with a brownish yellow coating of CADMIUM OXIDE, owing to the instant volatilization of the reduced metal and its subsequent reoxidation in passing through the oxidizing flame. The coating is seen most distinctly after cooling.

10. The *metallic incrustation*, obtained according to p. 33, is black with brown edge. The *incrustation of oxide* is brownish black, the edge passing from brown to white. The *incrustation of iodide* is white. The *incrustation of sulphide* is lemon-yellow, not dissolved by ammonium sulphide (BUNSEN).

§ 123.

Recapitulation and remarks.—The perfect separation of the metals of the second division of the fifth group from silver and mercurous salts may, as already stated, be effected by means of hydrochloric acid; but this agent fails to separate them completely from lead. Traces of mercuric salt, which are at first retained by the precipitated silver chloride by surface attraction, are dissolved out completely by washing (G. J. MULDER). MERCURIC compounds are distinguished from compounds of the other metals of this division by the insolubility of mercuric sulphide in boiling nitric acid. This property affords a convenient means for their separation. Care must always be taken to free the sulphides *completely* by washing from all traces of hydrochloric acid or a chloride that may happen to be present, before proceeding to boil them with nitric acid. Moreover, the reactions with stannous chloride or with metallic copper, as well as those in the dry way, will, after the previous removal of mercurous chloride, always readily indicate the presence of mercuric compounds. When the moist way is chosen, the mercuric sulphide is dissolved most conveniently by heating with hydrochloric acid and a crystal of potassium chlorate.

From the remaining metals LEAD is separated by sulphuric acid. The separation is the most complete if the fluid, after addition of dilute sulphuric acid in excess, is evaporated on the water-bath, the residue diluted with water slightly acidified with sulphuric acid, and the undissolved lead sulphate filtered off immediately. The lead sulphate may be further examined in the dry way by the reaction described in § 117, 10, or also as follows: Pour over a small portion of the lead sulphate a little of a solution of potassium chromate, and apply heat, which will convert the white precipitate into yellow lead chromate. Wash this, add a little solution of potassa or soda, and heat; the precipitate will now dissolve to a clear fluid; by acidifying this fluid with acetic acid, a yellow precipitate of lead chromate will again be produced. After the removal of mercury and lead, BISMUTH may be separated from copper and cadmium by addition of ammonia in excess, as the hydroxides of the latter two metals are soluble in an excess of this agent. If the precipitate, after being filtered off, is dis-

solved in one or two drops of hydrochloric acid on a watch-glass, and water added, the appearance of a milky turbidity is a confirmation of the presence of bismuth. The presence of a notable quantity of COPPER is revealed by the blue color of the ammoniacal solution; smaller quantities are detected by evaporating the ammoniacal solution nearly to dryness, adding a little acetic acid, and then potassium ferrocyanide. The separation of copper from CADMIUM may be effected by evaporating the ammoniacal solution to a small bulk, acidifying with hydrochloric acid, adding a little sulphurous acid and potassium sulphocyanate, filtering off the cuprous sulphocyanate, and precipitating the cadmium in the filtrate by hydrogen sulphide (an unnecessarily large excess of sulphurous acid must of course be avoided). The separation of copper from cadmium may also be effected by acting on the sulphides with potassium cyanide, or with boiling dilute sulphuric acid (5 parts of water to 1 part of concentrated acid). In the two latter methods the solution of copper and cadmium is precipitated by hydrogen sulphide, and the precipitate separated from the fluid by decantation or filtration. On treating the precipitate now with some water and a small lump of potassium cyanide, the cupric sulphide will dissolve, leaving the yellow cadmium sulphide undissolved. By boiling the precipitate of the mixed sulphides, on the other hand, with dilute sulphuric acid, the cupric sulphide remains undissolved, whilst the cadmium sulphide is obtained in solution. Hydrogen sulphide will therefore now throw down from the filtrate yellow cadmium sulphide (A. W. HOFMANN).

Special Reactions of the rarer Metals of the Fifth Group.

§ 124.

a. PALLADIUM, Pd. 106.6.

PALLADIUM is found in the metallic state, occasionally alloyed with gold and silver, but more particularly in platinum ores. It greatly resembles platinum, but is somewhat darker in color. It fuses with great difficulty. Heated in the air to dull redness it becomes covered with a blue film, but it recovers its light color and metallic lustre upon more intense ignition. It is sparingly soluble in pure nitric acid, but dissolves somewhat more readily in nitric acid containing nitrous acid; it dissolves very sparingly in boiling concentrated sulphuric acid, but it is soluble in fusing sodium disulphate, and readily soluble in

nitro-hydrochloric acid. There are three oxides, the suboxide (Pd_2O), the monoxide (Pd O), and the dioxide ($Pd O_2$). PALLADIUM MONOXIDE is black, the corresponding hydroxide dark brown; both are decomposed by intense ignition, leaving a residue of metallic palladium. PALLADIUM DIOXIDE is black; by heating with dilute hydrochloric acid it is dissolved to palladious chloride ($Pd Cl_2$), with evolution of chlorine. The PALLADIOUS SALTS are mostly soluble in water; they are brown or reddish-brown; their concentrated solutions are reddish-brown, their dilute solutions yellow. Water precipitates from a solution of palladious nitrate containing a slight excess of acid a brown basic salt. The oxysalts, as well as palladious chloride, are decomposed by ignition, leaving metallic palladium behind. *Hydrogen sulphide* and *ammonium sulphide* throw down from acid or neutral solutions black palladious sulphide, which does not dissolve in ammonium sulphide, but is soluble in boiling hydrochloric acid, and readily soluble in nitro-hydrochloric acid. From the solution of palladious chloride *potassa* precipitates a brown basic salt, soluble in an excess of the precipitant; *ammonia*, flesh-colored ammonio-palladium chloride ($Pd Cl_2 . 2 N H_3$) soluble in excess of ammonia to a colorless fluid, from which hydrochloric acid throws down yellow crystalline palladammonium chloride ($N_2Pd H_6Cl_2$). *Mercuric cyanide* throws down yellowish-white palladious cyanide as a gelatinous precipitate, slightly soluble in hydrochloric acid, readily soluble in ammonia (especially characteristic). *Stannic chloride* produces, in absence of free hydrochloric acid, a brownish-black precipitate; in presence of free hydrochloric acid, a red-colored solution, which speedily turns brown and ultimately green, and upon addition of water brownish-red. *Ferrous sulphate* produces a deposit of palladium on the sides of the glass. *Potassium iodide* precipitates black palladious iodide (very characteristic). *Potassium chloride* precipitates from highly concentrated solutions potassium palladious chloride ($2K Cl . Pd Cl_2$), in the form of golden-yellow needles, which dissolve readily in water to a dark red fluid, but are insoluble in absolute alcohol. *Potassium nitrite* produces in not too dilute solutions a yellowish crystalline precipitate, which becomes reddish on long standing and is soluble in much water. *Potassium sulphocyanate* does not precipitate palladium, even after the addition of sulphurous acid (difference from copper, and best means of separating from the same). On treatment with *sodium carbonate* in the upper oxidizing flame (p. 30) all the compounds of palladium yield a gray metallic sponge.

b. RHODIUM, Rh. 104.4.

RHODIUM is found in small quantity in platinum ores. It is almost silver white, very malleable, and difficultly fusible. When prepared in the wet way it is a gray powder. The powder when ignited in the air absorbs oxygen, which it gives up again upon stronger ignition. Rhodium is insoluble in all acids; it dissolves in aqua regia only when alloyed with platinum, copper, etc., and not when alloyed with gold or silver. Fusing metaphosphoric acid and fusing potassium disulphate dissolve it, forming a rhodic salt. There are four oxides: the monoxide (Rh O), rhodic oxide (Rh_2O_3) (base of the salts), dioxide ($Rh O_2$), and trioxide ($Rh O_3$) (a weak acid). RHODIC OXIDE is gray, it yields a yellow and a brownish-black hydroxide; it is insoluble in acids, but dissolves in fusing metaphosphoric acid and in fusing sodium disulphate. The

solutions are rose-colored. *Sulphuretted hydrogen* and *ammonium sulphide* precipitate in time, especially when assisted by heat, brown rhodic sulphide, which is insoluble in ammonium sulphide, but dissolves in boiling nitric acid. *Potassa*, if added in not too large excess, throws down at once yellow Rh (O H)$_3$ H_2O, which is soluble in excess of the precipitant at the ordinary temperature ; on boiling the solution, blackish-brown Rh (O H)$_3$ is precipitated. In a solution of rhodic chloride, potassa at first produces no precipitate, but, on addition of alcohol, black Rh (O H)$_3$ separates soon (CLAUS). *Ammonia* produces after some time a yellow precipitate, soluble in hydrochloric acid. *Zinc* precipitates black metallic rhodium. On heating with *potassium nitrite*, rhodic chloride becomes yellow, and an orange-yellow precipitate is formed, which is slightly soluble in hydrochloric acid ; at the same time another portion of the rhodium is converted into a yellow salt, which remains in solution and is precipitated by alcohol (GIBBS). All solid compounds of rhodium, on ignition in *hydrogen*, or on ignition on a platinum wire with *sodium carbonate* in the upper oxidizing flame, yield the metal, which is well characterized by its insolubility in aqua regia, its solubility in fusing potassium disulphate, and the behavior of its solution to potassa and alcohol.

c. OSMIUM, Os. 199.2.

OSMIUM is found in platinum ores as a native alloy of osmium and iridium. It is generally obtained as a black powder, or gray and with metallic lustre ; it is infusible. The metal, the HYPO-OSMIOUS OXIDE (Os O), and the OSMIC OXIDE (Os O_2) oxidize readily when heated to redness in the air, and give OSMIUM TETROXIDE (Os O_4), which volatilizes and makes its presence speedily known by its peculiar exceedingly irritating and offensive smell, resembling that of chlorine and iodine (highly characteristic). If a little osmium on a strip of platinum foil is held in the outer mantle of a *gas or alcohol flame*, at half height, the flame becomes most strikingly luminous. Even minute traces of osmium may by this reaction be detected in alloys of iridium and osmium ; but the reaction is in that case only momentary ; it may however be reproduced by holding the sample first in the reducing flame, then again in the outer mantle. *Nitric acid*, more particularly red fuming nitric acid, and aqua regia dissolve osmium to tetroxide. Application of heat promotes the solution, which is however attended in that case with volatilization of tetroxide. Very intensely ignited osmium is insoluble in acids. On fusing with potassium nitrate and distilling the fused mass with nitric acid, osmium tetroxide is found in the distillate. By heating osmium in dry *chlorine* free from air, first bluish-black HYPO-OSMIOUS CHLORIDE (Os Cl_2) is formed, but always only in small quantity, then the more volatile and red OSMIC CHLORIDE (Os Cl_4) ; if moist chlorine is used, a green mixture of both chlorides is formed. The hypo-osmious chloride dissolves with a blue color, the osmic chloride with a yellow color, and both together with a green color, which turns red. The solutions are soon decomposed, osmium tetroxide, hydrochloric acid, and a mixture of hypo-osmious and osmic oxides being formed, the mixed oxides separating as a black powder. On heating a mixture of powder of osmium, or osmium sulphide and potassium chloride in chlorine, a double salt of POTASSIUM HYPO-OSMIOUS CHLORIDE is produced in the form of octahedra, which are slightly soluble in water and insoluble in alcohol. The solution of this

double salt is more permanent than that of the hypo-osmious chloride Potassa decolorizes the solution; on boiling, bluish-black OSMIC HYDROXIDE $Os(OH)_4$ separates. On fusing the double chloride with sodium carbonate, dark gray OSMIC OXIDE separates. Osmium tetroxide is white, crystalline, fusible at a gentle heat, and boils at about 100°; the fumes attack the nose and eyes powerfully. Heated with water, it fuses and dissolves, but slowly. The solution has an irritating, unpleasant smell. *Alkalies* color the solution yellow in consequence of the formation of osmites (*e.g.*, $K_2 Os O_4 . 2 H_2 O$); on distilling, the greater part of the osmium passes over as tetroxide (very characteristic), the remainder gives off oxygen, leaving an osmite, or on boiling, splits into osmium tetroxide, osmic oxide, and potassa. Osmium tetroxide decolorizes *indigo solution*, separates iodine from *potassium iodide*, converts *alcohol* into aldehyde and acetic acid. *Potassium nitrite* readily reduces it to potassium osmite. *Hydrogen sulphide* precipitates brownish-black sulphide, which only separates when a strong acid is present; the precipitate is insoluble in ammonium sulphide. *Sodium sulphite* produces a deep violet coloration, and dark-blue hypo-osmious sulphite gradually separates, especially on evaporating or warming with sodium sulphate or carbonate. *Ferrous sulphate* produces a black precipitate of osmic oxide. *Stannous chloride* produces a brown precipitate, soluble in hydrochloric acid to a brown fluid. *Zinc* and many metals in the presence of a strong acid precipitate metallic osmium. All the compounds of osmium yield the metal on ignition in a current of *hydrogen*.

d. RUTHENIUM, Ru. 104.4.

RUTHENIUM is found in small quantity in platinum ores. It is a grayish-white, brittle, and very difficultly fusible metal. It is barely acted upon by aqua regia; fusing sodium disulphate fails altogether to affect it. By ignition in the air it is converted into bluish-black ruthenious oxide, $Ru_2 O_3$, insoluble in acids; by ignition with potassium chloride in a current of chlorine gas into potassium ruthenious chloride, by fusion with potassium nitrate, with potassa, or with potassium chlorate into potassium ruthenate, $K_2 Ru O_4$. The fused mass obtained in the latter case is greenish-black, and dissolves to an orange-colored fluid, which tinges the skin black from separation of black oxide. Acids throw down from the solution black RUTHENIOUS OXIDE, which dissolves in hydrochloric acid to an orange-yellow fluid containing RUTHENIOUS CHLORIDE, $Ru_2 Cl_3$. This solution is resolved by heat into hydrochloric acid and ruthenious oxide. In a concentrated state it gives with potassium chloride and ammonium chloride crystalline glossy violet precipitates (*e.g.*, potassium ruthenious chloride, $Ru_2 Cl_6 . 4 K Cl$), which on boiling with water deposit a black oxychloride. *Potassa* precipitates black ruthenious hydroxide, $Ru(OH)_3$, which is insoluble in alkalies, but dissolves in acids. *Hydrogen sulphide* causes at first no alteration; but after some time the fluid acquires an azure-blue tint, and deposits brown ruthenium sulphide (very characteristic). *Ammonium sulphide* produces brownish-black precipitates, barely soluble in an excess of the precipitant. *Potassium sulphocyanate* produces—in the absence of other metals of the platinum ores—after some time a red coloration, which gradually changes to purple-red, and upon heating to a fine violet tint (very characteristic). *Zinc* produces at first an azure-blue coloration, which subsequently disappears, ruthenium being deposited at the same time in the metallic

state. *Potassium nitrite* colors the solution yellow, with the formation of a double salt, which is readily soluble in water and alcohol. The alkaline solution of this double salt, when mixed with a little colorless ammonium sulphide turns crimson (characteristic); on the addition of more ammonium sulphide, ruthenium sulphide is precipitated.

§ 125.

SIXTH GROUP.

More common elements: GOLD, PLATINUM, TIN, ANTIMONY, ARSENIC.

Rarer elements: IRIDIUM, MOLYBDENUM, TUNGSTEN, TELLURIUM, SELENIUM.

The higher hydroxides of the elements belonging to the sixth group have all of them more or less strongly pronounced acid characters. But we class them here, as they cannot be well separated from the lower oxides and hydroxides of the same elements, to which they are very closely allied in their reactions with hydrogen sulphide.

Properties of the group.—The sulphides of the elements of the sixth group are insoluble in dilute acids. These sulphides combine with alkali sulphides (either immediately, or with the aid of sulphur) to soluble sulphur salts, in which they take the part of the acid. Hydrogen sulphide precipitates these elements therefore, like those of the fifth group, completely from acidified solutions. The precipitated sulphides differ, however, from those of the fifth group in this, that they dissolve in ammonium sulphide, potassium sulphide, etc., and are precipitated from these solutions by addition of acids.

We divide the more common metals of this group into two classes, and distinguish,

1. METALS WHOSE SULPHIDES ARE INSOLUBLE IN HYDROCHLORIC ACID AND IN NITRIC ACID, and are reduced to the metallic state upon fusion with sodium nitrate and carbonate, viz., GOLD and PLATINUM.

2. METALS WHOSE SULPHIDES ARE SOLUBLE IN BOILING HYDROCHLORIC ACID OR NITRIC ACID, and are upon fusion with sodium nitrate and carbonate converted into sodium salts: viz., ANTIMONY, TIN, and ARSENIC.

FIRST DIVISION.

Special Reactions.

§ 126.

a. GOLD, Au. 197.

1. METALLIC GOLD has a reddish-yellow color and a high metallic lustre; it is rather soft, exceedingly malleable, difficultly fusible; it does not oxidize upon ignition in the air, and is insoluble in hydrochloric, nitric, and sulphuric acids; but it dissolves in fluids containing or evolving chlorine, *e.g.*, in nitro-hydrochloric acid. The solution contains hydrochlorauric acid, $H\,Au\,Cl_4$.

2. AURIC OXIDE ($Au_2\,O_3$) is a blackish-brown powder. AURIC HYDROXIDE (AURIC ACID), $Au\,O.OH$, is a chestnut-brown powder. Both are reduced by light and heat, and dissolve readily in hydrochloric acid, but not in dilute oxygen acids. Concentrated nitric and sulphuric acids dissolve a little auric oxide; water reprecipitates it from these solutions; auric hydroxide dissolves in potassa with formation of potassium aurate, $K\,Au\,O_2 + 3\,H_2\,O$. AUROUS OXIDE; $Au_2\,O$, is violet black; it is decomposed by heat into gold and oxygen.

3. OXYGEN SALTS of gold are little known. The HALOID SALTS are yellow, and their solutions exhibit this color at a high degree of dilution. The whole of them are readily decomposed by ignition. Hydrochlorauric acid reddens litmus paper, and when heated loses hydrochloric acid and chlorine, leaving a residue consisting of auric chloride, $Au\,Cl_3$, aurous chloride, $Au\,Cl$, or metallic gold, according to the temperature.

4. *Hydrogen sulphide* precipitates from neutral or acid solutions the whole of the metal, from cold solutions as AURIC SULPHIDE, $Au_2\,S_3$, from boiling solutions as AUROUS SULPHIDE, $Au_2\,S$. The precipitates are insoluble in hydrochloric and in nitric acid, but soluble in nitro-hydrochloric acid. They are insoluble in colorless ammonium sulphide, but soluble in yellow ammonium sulphide, and more readily still in yellow sodium sulphide or potassium sulphide.

5. *Ammonium sulphide* precipitates brownish-black AURIC SULPHIDE, which redissolves in an excess of the precipitant only if the latter contains an excess of sulphur.

6. *Ammonia* produces, though only in concentrated solutions of gold, reddish-yellow precipitates of *fulminating gold*. The more acid the solution and the greater the excess of ammonia added, the more gold remains in solution.

7. *Stannous chloride*, containing an admixture of *stannic chloride* (which may be easily prepared by mixing solution of stannous chloride with a little chlorine water) produces, even in extremely dilute solutions of gold, a purple-red precipitate (or coloration at least), which sometimes inclines rather

to violet or to brownish-red. This precipitate, which has received the name of PURPLE OF CASSIUS, is insoluble in hydrochloric acid. Its constitution is not established.

8. *Ferrous salts* reduce hydrochlorauric acid solutions, and precipitate METALLIC GOLD in form of a most minutely divided brown powder. The fluid in which the precipitate is suspended appears of a blackish-blue color by transmitted light. The dried precipitate shows metallic lustre when pressed with the blade of a knife.

9. *Potassium nitrite* produces a precipitate of metallic gold. In very dilute solutions the fluid at first only appears colored blue, but in time the whole of the gold separates.

10. *Potassa* or *soda* added in excess to hydrochlorauric acid leaves the fluid clear, but upon addition of *tannic acid* metallic gold separates. Warming assists the precipitation.

11. All compounds of gold are reduced in the *stick of charcoal* (p. 31). By triturating the charcoal afterwards, yellow spangles of metal will be obtained, which are insoluble in nitric acid, but readily soluble in aqua regia.

§ 127.

b. PLATINUM, Pt. 197.4.

1. METALLIC PLATINUM has a light steel-gray color; it is very lustrous, moderately hard, very difficultly fusible; it does not oxidize upon ignition in the air, and is insoluble in hydrochloric, nitric, and sulphuric acids. It dissolves in nitro-hydrochloric acid, especially upon heating. The solution contains hydrochloroplatinic acid.

2. PLATINIC OXIDE, PtO_2, is a blackish-brown powder. PLATINIC HYDROXIDE (PLATINIC ACID) $Pt(OH)_4$ is a reddish-brown powder. Both are reduced by heat; they are both readily soluble in hydrochloric acid, and difficultly soluble in oxygen acids PLATINOUS OXIDE, PtO, is black; PLATINOUS HYDROXIDE, $Pt(OH)_2$, brown; they are both by ignition reduced to the metallic state.

3. The PLATINIC SALTS are yellow, and are decomposed at a red heat. HYDROCHLOROPLATINIC ACID, H_2PtCl_6, is reddish-brown, its solution reddish yellow, which tint it retains up to a high degree of dilution. The solution reddens litmus paper. Exposure to a very low red heat converts hydrochloroplatinic acid into platinous chloride, $PtCl_2$; application of a stronger red heat reduces it to metal. Solution of hydrochloroplatinic acid, containing platinous chloride, has a deep brown color.

4. *Hydrogen sulphide* throws down from acid and neutral platinic solutions, but always only after the lapse of some

time, a blackish-brown precipitate of PLATINIC SULPHIDE, PtS_2. If the solution is heated after the addition of the hydrogen sulphide, the precipitate forms immediately. It dissolves in a great excess of alkali sulphides, more particularly of the higher degrees of sulphuration. Platinic sulphide is insoluble in hydrochloric acid and in nitric acid; but it dissolves in nitro-hydrochloric acid.

5. *Ammonium sulphide* produces the same precipitate; this redissolves completely, though slowly and with difficulty, in a large excess of the precipitant if the latter contains an excess of sulphur. Acids reprecipitate the platinic sulphide unaltered from the reddish-brown solution.

6. *Potassium chloride* and *ammonium chloride* (and accordingly also potassa and ammonia in presence of hydrochloric acid) produce in not too highly dilute solutions of hydrochloroplatinic acid yellow crystalline precipitates of POTASSIUM and AMMONIUM PLATINICHLORIDE, which are as insoluble in acids as in water, but are dissolved by heating with solution of potassa. From dilute solutions these precipitates are obtained by evaporating the fluid mixed with the precipitants on the water-bath, and treating the residue with a little water or with dilute spirit of wine. Upon ignition ammonium platinichloride leaves spongy platinum behind; potassium platinichloride leaves platinum and potassium chloride. The decomposition of potassium platinichloride is complete only if the ignition is effected in a current of hydrogen gas, or with addition of some oxalic acid.

7. *Stannous chloride* imparts to platinic solutions containing much free hydrochloric acid an intensely dark brownish-red color, owing to a reduction of the hydrochloroplatinic acid to platinous chloride. But the reagent produces no precipitate in such solutions.

8. *Ferrous sulphate* does not precipitate solution of hydrochloroplatinic acid, except upon very long-continued boiling, in which case the platinum ultimately suffers reduction.

9. On igniting a compound of platinum mixed with *sodium carbonate* on the loop of a platinum wire in the upper *oxidizing flame*, a gray spongy mass is obtained, which on trituration in an agate mortar yields silvery spangles, insoluble in hydrochloric and nitric acid, but soluble in aqua regia.

§ 128.

Recapitulation and remarks.—The reactions of gold and platinum enable us, in many cases, to detect those two metals directly in the presence of many others. Where platinum and gold are present in the same solution, the liquid is most conveniently evaporated to dryness at a gentle heat with ammonium chloride, and the residue treated with dilute alcohol, in order to obtain the gold in solution and the platinum in the residue. The precipitate will thus give platinum by ignition, and the gold may be precipitated from the solution by ferrous sulphate, after removing the alcohol by evaporation.

SECOND DIVISION.

Special Reactions.

§ 129.

a. TIN,* Sn. 118, AND STANNOUS COMPOUNDS.

1. TIN has a light grayish-white color and a high metallic lustre; it is soft and malleable; when bent it produces a crackling sound. Heated in the air it absorbs oxygen and is converted into grayish-white stannic oxide; heated on charcoal before the blowpipe it forms a white incrustation. Tin dissolves with difficulty in dilute sulphuric acid; concentrated sulphuric acid converts it, with the aid of heat, into stannic sulphate.

Concentrated hydrochloric acid dissolves tin to stannous chloride, with evolution of hydrogen gas; nitro-hydrochloric acid dissolves it, according to circumstances, to stannic chloride or to a mixture of stannous and stannic chlorides. Moderately concentrated nitric acid oxidizes it readily, particularly with the aid of heat; the white hydroxide formed (metastannic acid, $Sn_5 H_{10} O_{15}$?) does not redissolve in an excess of the nitric acid.

2. STANNOUS HYDROXIDE, $Sn H_2 O_2$, is white. By ignition in carbon dioxide it yields STANNOUS OXIDE, Sn O, as a black or grayish-black powder. Stannous oxide is reduced to metal by fusion with potassium cyanide, it is readily soluble in hydrochloric acid. Nitric acid converts it into metastannic acid, which is insoluble in an excess of the acid.

3. The STANNOUS SALTS are colorless; they are decomposed by heat. The

* In the stannous compounds tin is bivalent, in the stannic compounds it is quadrivalent.

soluble normal salts redden litmus paper. The stannous salts rapidly absorb oxygen from the air, and are partially or entirely converted into stannic salts. Stannous chloride, no matter whether in crystals or in solution, also absorbs oxygen from the air, which leads to the formation of insoluble stannous oxychloride and stannic chloride. Hence a solution of stannous chloride becomes speedily turbid if the bottle is often opened and there is only little free acid present; and hence it is only quite recently prepared stannous chloride which will completely dissolve in water free from air, whilst crystals of stannous chloride that have been kept for any time will dissolve to a clear fluid only in water containing hydrochloric acid.

4. *Hydrogen sulphide* throws down from neutral and acid solutions a dark brown precipitate of STANNOUS SULPHIDE, Sn S. This reagent does not precipitate alkaline solutions, or at least not completely. The precipitation may be prevented by the presence of a very large quantity of free hydrochloric acid. The precipitate is insoluble, or nearly so, in colorless ammonium sulphide, but dissolves readily in the yellow sulphide, as ammonium sulphostannate, $(NH_4 S)_2 Sn S$. Acids precipitate from this solution yellow stannic sulphide, mixed with sulphur. Stannous sulphide dissolves also in solutions of soda and potassa. Acids precipitate it again from these solutions unaltered. Boiling hydrochloric acid dissolves it, with evolution of hydrogen sulphide; boiling nitric acid converts it into insoluble metastannic acid.

5. *Ammonium sulphide* produces the same precipitate of STANNOUS SULPHIDE.

6. *Potassa, soda, ammonia,* and *carbonates of the alkali metals* produce a white bulky precipitate of STANNOUS HYDROXIDE, $Sn H_2 O_2$, which redissolves readily in an excess of potassa or soda, but is insoluble in an excess of the other precipitants. If the solution of stannous hydroxide in potassa (potassium stannite) is briskly evaporated, potassium stannate, $Sn O (O K)_2$ is formed, which remains in solution, whilst metallic tin precipitates; but upon evaporating slowly crystalline stannous oxide separates.

7. *Hydrochlorauric acid* produces in solutions of stannous chloride and in solutions of other stannous salts mixed with hydrochloric acid a precipitate which varies in color between brown, reddish-brown, and purple-red, according to the presence of more or less stannic chloride and the state of concentration (compare § 126, 7). In very dilute solutions a more or less brown or red coloration merely is produced.

8. Solution of *mercuric chloride*, added in excess, to solutions of stannous chloride or of a stannous salt mixed with hydrochloric acid, produces a white precipitate of MERCUROUS CHLORIDE, owing to the stannous salt withdrawing from the mercuric chloride half of its chlorine.

9. If a fluid containing a stannous salt and hydrochloric acid is added to a mixture of *potassium ferricyanide* and *ferric chloride* a precipitate of PRUSSIAN BLUE separates immediately. This reaction is extremely delicate, but it can be held to be decisive only in cases where no other reducing agent is present.

10. *Zinc* precipitates from solutions mixed with hydrochloric acid METALLIC TIN in the form of gray laminæ or of a spongy mass. If the experiment is made in a platinum capsule, the latter is not colored black.

11. If stannous compounds, mixed with *sodium carbonate* and some *borax*, or better still, with a mixture of equal parts of *sodium carbonate* and *potassium cyanide*, are exposed on a charcoal support to the *inner blowpipe flame*, malleable grains of METALLIC TIN are obtained on cutting out and forcibly triturating the surrounding parts of charcoal with water in a small mortar, and washing off the charcoal from the metallic particles. Upon strongly heating the grains of metallic tin on a charcoal support the latter becomes covered with a coating of white stannic oxide. The stick of charcoal (p. 31) is also admirably adapted for the reduction of tin.

12. If, to a borax bead colored slightly blue by copper, a trace of a stannous compound is added and the bead is heated in the *lower reducing flame* of the gas lamp (p. 30), it will become reddish-brown to ruby-red in consequence of the formation and separation of cuprous oxide (compare § 120, 14). A compound of tin is essential to this reaction.

§ 130.

b. TIN, Sn. 118. STANNIC COMPOUNDS.

1. STANNIC OXIDE, SnO_2, is a powder varying in color from white to straw-yellow, and which upon heating transiently assumes a brown tint. The HYDROXIDE precipitated by alkalies from solution of stannic chloride (obtained by heating tin in chlorine gas, or by dissolving it in aqua regia), dissolves readily in hydrochloric acid—it is STANNIC ACID, SnH_2O_3. The HYDROXIDE formed by the action of nitric acid upon tin—METASTANNIC ACID ($Sn_5H_{10}O_{15}$?)—remains undissolved. But if metastannic acid is boiled for some time with hydrochloric acid it takes up chlorine; if the excess of the acid is then poured off and water added, a clear solution of metastannic chloride is obtained. The aqueous solution of the stannic chloride is not precipitated by concentrated hydrochloric acid, whilst the acid produces in the aqueous solution of the metastannic chloride a white precipitate of the latter compound. The solution of stannic chloride is not colored yellow by addition of stannous chloride, as is the case in a remarkable degree if the solution contains metastannic chloride (LÖWENTHAL). The dilute solutions of both chlorides give upon boiling precipitates of the hydroxides corresponding to the chlorides.

2. The STANNIC SALTS are mostly colorless, but stannic iodide is orange-red.

The soluble salts are decomposed at a red heat; they redden litmus paper. STANNIC CHLORIDE, $Sn Cl_4$, is a volatile liquid, strongly fuming in the air.

3. *Hydrogen sulphide* throws down from all acid and neutral stannic solutions, particularly upon heating, a white flocculent precipitate if the stannic solution is in excess; a dull yellow precipitate if the hydrogen sulphide is in excess. The former, in the case of a solution of stannic chloride, probably consists of a mixture of stannic chloride and stannic sulphide (it has not however as yet been analyzed); the latter consists of STANNIC SULPHIDE $Sn S_2$. Alkaline solutions are not precipitated by hydrogen sulphide. Presence of a very large quantity of hydrochloric acid may prevent precipitation. Stannic sulphide dissolves readily in potassa or soda, alkali sulphides, and concentrated boiling hydrochloric acid, as also in aqua regia. It dissolves with some difficulty in ammonia, is nearly insoluble in ammonium carbonate, and insoluble in hydrogen potassium sulphite. Concentrated nitric acid converts it into insoluble metastannic acid. Upon deflagrating stannic sulphide with sodium nitrate and carbonate, sodium sulphate and stannic oxide are obtained. If a solution of stannic sulphide in potassa (potassium sulphostannate, $Sn S (K S)_2$) is boiled with bismuth trioxide, insoluble bismuth trisulphide and soluble potassium stannate are formed.

4. *Ammonium sulphide* produces the same precipitate of STANNIC SULPHIDE; the precipitate redissolves readily in an excess of the precipitant, as ammonium sulphostannate. From this solution acids reprecipitate the stannic sulphide unaltered.

5. *Potassa, soda,* and *ammonia, sodium* and *ammonium carbonates* produce white precipitates which, according to the nature of the solutions, consist of stannic acid, or of metastannic acid. The former readily dissolves in a slight excess of potassa, slightly in a large excess; on the other hand, it dissolves only after considerable dilution in a slight excess of soda, and on the addition of more soda almost all the stannic acid separates again. The latter is hardly soluble in excess of potassa or soda.

6. *Sodium sulphate* or *ammonium nitrate*—in fact, most normal alkali salts, when added in excess—throw down from stannic or metastannic solutions, provided they are not too acid, the whole of the tin as STANNIC ACID or METASTANNIC ACID. Heating promotes the precipitation: $Sn Cl_4 + 4 (Na_2 S O_4) + 3 H_2 O = Sn H_2 O_3 + 4 Na Cl + 4 (Na H S O_4)$.

7. *Metallic zinc* precipitates from solutions of stannic or metastannic chloride, in the presence of free acid, METALLIC

TIN in the shape of small gray scales, or as a spongy mass. If the operation is conducted in a platinum dish, no blackening of the latter is observed (difference between tin and antimony).

8. The stannic and metastannic compounds show the same reactions before the *blowpipe* or in the *gas flame* as the stannous compounds. Stannic oxide is also readily reduced when fused with potassium cyanide in a glass tube or in a crucible.

§ 131.

c. ANTIMONY, Sb. 122.

1. METALLIC ANTIMONY has a bluish tin-white color, and is lustrous; it is hard, brittle, readily fusible, volatile at a very high temperature. When heated on charcoal before the blowpipe it emits thick white fumes of antimonious oxide, which form a coating on the charcoal; this combustion continues for some time, even after the removal of the metal from the flame; it is the most distinctly visible if a strong current of air is thrown by the blowpipe directly upon the sample on the charcoal. But if the fumes ascend straight, the hot metallic bead becomes surrounded with a net of brilliant acicular crystals of antimonious oxide.

Nitric acid oxidizes antimony readily; the dilute acid converts it almost entirely into antimonious oxide; the more concentrated the acid the more metantimonic acid is formed; boiling concentrated acid converts it almost completely into metantimonic acid. Neither of the two is altogether insoluble in nitric acid; traces of antimony are therefore always found in the acid fluid filtered from the precipitate. Hydrochloric acid, even boiling, does not attack antimony. In nitro-hydrochloric acid the metal dissolves readily. The solution contains antimonious chloride, $SbCl_3$, or antimonic chloride $SbCl_5$, according to the degree of concentration of the acid and the duration of the action.

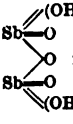
2. According to the mode of its preparation ANTIMONIOUS OXIDE (Sb_2O_3) occurs in white and brilliant crystalline needles, or as a white powder. It fuses at a moderate red heat in a closed vessel; at a higher temperature it volatilizes without decomposition. It is almost insoluble in nitric acid, but dissolves readily in hydrochloric and tartaric acids. No separation of iodine takes place on boiling it with hydrochloric acid (free from chlorine) and potassium iodide (free from iodic acid). BUNSEN. Antimonious oxide is easily reduced to metal by fusion with potassium cyanide.

3. METANTIMONIC ACID ($Sb O_3 O H$),* produced by the action of concentrated nitric acid on antimony and PYROANTIMONIC ACID ($Sb_2 O_7 H_4$?),† which is formed when antimonic chloride is treated with much water, are white. They both redden moist litmus paper; they are only very sparingly soluble in water, and almost insoluble in nitric acid, but dissolve pretty readily in hot concentrated hydrochloric acid; the solution contains ANTIMONIC CHLORIDE ($Sb Cl_5$) and turns turbid upon addition of water. On boiling metantimonic acid with hydrochloric acid and potassium iodide, iodine separates which dissolves in the hydriodic acid present to a brown fluid (BUNSEN). Upon heating metantimonic acid or pyroantimonic acid, just short of redness ANTIMONIC OXIDE (Sb_2O_5) is obtained as a yellow powder insoluble in water and acids. By stronger ignition the latter loses oxygen, and is converted into infusible ANTIMONIOUS ANTIMONATE or antimony tetroxide ($Sb_2 O_4$). Of the metantimonates and pyroantimonates the potassium and ammonium salts are almost the only ones soluble in water. Potassium metantimonate ($Sb O_3 K$), obtained by fusing antimony or its sulphides with nitre, is a white mass nearly insoluble in cold water. On boiling with water it gradually dissolves to the readily soluble orthoantimonate ($Sb O_4 H_2 K$). On fusing either of the above salts, or metantimonic acid with a large excess of potassa, a mass is obtained which readily dissolves in water. From the solution by evaporation crystals of potassium pyroantimonate ($Sb_2 O_7 K_4$) may be obtained, which are only permanent in presence of excess of potassa, and are decomposed by water into potassa and hydrogen potassium pyroantimonate ($Sb_2 O_7 H_2 K_2$) (§ 54).

The sodium metantimonates are nearly, the sodium pyroantimonates are quite insoluble in water. The soluble potassium antimonates are accordingly precipitated by sodium chloride (§ 90, 2). On treating metantimonates and pyroantimonates with acids, metantimonic and pyroantimonic acids are precipitated.

4. The greater part of the ANTIMONIOUS SALTS are decomposed upon ignition; the haloid salts volatilize readily and unaltered. The soluble normal antimony salts redden litmus paper. With a large quantity of water they are decomposed with formation of insoluble basic salts and separation of free acid. Thus, for instance, *water* throws down from solutions of antimonious chloride in hydrochloric acid a white bulky precipitate of ANTIMONIOUS OXYCHLORIDE (powder of Algaroth), which soon becomes heavy and crystalline. $4 Sb Cl_3 + 5 H_2 O = 2 (Sb O Cl) Sb_2 O_3 + 10 H Cl$. Tartaric acid dissolves this precipitate readily, and therefore prevents

* Or H, antimonic acid of former editions.

†  metantimonic acid of former editions.

its formation if mixed with the solution previously to the addition of the water. It is by this property that this antimony compound is distinguished from the basic bismuth salts formed under similar circumstances.

5. *Hydrogen sulphide* precipitates from acid solutions (if the quantity of free mineral acid present is not too large) the whole of the metal as orange-red amorphous ANTIMONIOUS SULPHIDE (Sb_2S_3). In alkaline solutions this reagent fails to produce a precipitate, or, at least, it precipitates them only imperfectly; neutral solutions also are only imperfectly thrown down by it. The antimonious sulphide produced is readily dissolved by potassa and by alkali sulphides, especially if the latter contain an excess of sulphur. Concentrated boiling hydrochloric acid dissolves it with evolution of hydrogen sulphide. By deflagration with sodium nitrate it gives sodium sulphate and sodium metantimonate. Sodium metantimonate is very sparingly soluble in water, and still less soluble in diluted alcohol, but readily soluble in strong hydrochloric acid.

Antimonious sulphide is but sparingly soluble in ammonia, and, if free from antimonic sulphide, almost insoluble in hydrogen ammonium carbonate. It is insoluble in dilute acids, as also in hydrogen potassium sulphite. By heating in the air it is converted into a mixture of antimony tetroxide with antimonious sulphide. If a potassa solution of antimonious sulphide (containing potassium sulphantimonite) is boiled with bismuth trioxide, bismuth trisulphide precipitates, and potassium orthoantimonate remains in the solution. On fusing antimonious sulphide with potassium cyanide, metallic antimony and potassium sulphocyanate are produced. If the operation is conducted in a small tube expanded into a bulb at the lower end, or in a stream of carbon dioxide (see § 132, 13), no sublimate of antimony is produced. But if a mixture of antimonious sulphide with sodium carbonate or with potassium cyanide and sodium carbonate is heated in a glass tube in a stream of hydrogen gas, a mirror of antimony is deposited in the tube, immediately behind the spot occupied by the mixture.

From a solution of antimonic acid in hydrochloric acid sulphuretted hydrogen throws down ANTIMONIC SULPHIDE (Sb_2S_5) mixed with antimonious sulphide and sulphur. The precipitate dissolves readily when heated with solution of soda or ammonia (forming, *e.g.*, sodium sulphantimonate, Na_3SbS_4) and equally so in concentrated boiling hydrochloric acid with evolution of hydrogen sulphide and separation of sulphur, but dissolves only very sparingly in cold solution of hydrogen ammonium carbonate.

6. *Ammonium sulphide* produces in solutions of antimonious salts an orange-red precipitate of ANTIMONIOUS SULPHIDE, which readily redissolves in an excess of the precipitant if

the latter contains an excess of sulphur, with formation of ammonium sulphantimonate. Acids throw down from this solution antimonic sulphide. However, the orange color appears in that case usually of a lighter tint, owing to an admixture of free sulphur.

7. *Potassa, soda, ammonia, sodium carbonate,* and *ammonium carbonate* throw down from solutions of antimonious chloride, and also of simple antimonious salts—but far less completely, and mostly only after some time, from solutions of tartar emetic or analogous compounds—a white bulky precipitate of ANTIMONIOUS HYDROXIDE, which redissolves pretty readily in an excess of potassa or soda, but requires the application of heat for its re-solution in sodium carbonate, and is almost insoluble in ammonia.

8. *Metallic zinc* precipitates from all solutions of antimonious oxide, if they contain no free nitric acid, METALLIC ANTIMONY as a black powder. If a few drops of a solution of antimony, containing some free hydrochloric acid, are put into a platinum capsule (the lid of a platinum crucible), and a fragment of zinc is introduced, hydrogen containing antimonetted hydrogen is evolved and antimony separates, staining the part of the platinum covered by the liquid brown or black, even in the case of very dilute solutions: this reaction is equally delicate and characteristic. Cold hydrochloric acid fails to remove the stain, heating with nitric acid removes it immediately.

9. If a solution of antimonious oxide in solution of soda (sodium antimonite) is mixed with solution of *silver nitrate*, a deep black precipitate of ARGENTOUS OXIDE forms with the grayish-brown precipitate of argentic oxide. Upon now adding ammonia in excess, the argentic oxide is redissolved, whilst the argentous oxide is left undissolved (H. ROSE). The formation of the argentous oxide in this process is explained as follows: $Na\ Sb\ O_2 + 2\ Ag_2\ O = Na\ Sb\ O_3 + Ag_4\ O$. This exceedingly delicate reaction affords an excellent means of detecting antimonious oxide or antimonites in presence of antimonic acid.

10. If any solution of antimony in hydrochloric or sulphuric acid is introduced into a flask in which hydrogen gas is being evolved from pure *zinc* and diluted *sulphuric acid* a portion of the antimony separates in the metallic state; but another portion of the metal combines with hydrogen, forming ANTIMONETTED HYDROGEN GAS ($Sb\ H_3$). If this operation is conducted in a gas-evolution flask, connected by means of a perforated cork with a bent tube ending in a jet,* and the hydrogen passing through the jet is ignited after the atmospheric air is completely expelled, the flame appears of a bluish-green tint, which is imparted to it by the antimony separating and burning in the flame. White fumes of antimonious oxide rise from the flame, which condense

* In accurate experiments it is advisable to use MARSH'S apparatus (§ 138, 10). By the employment of a platinum jet rolled from a bit of thin foil and inserted in the end of the glass delivery tube, the color of the flame will be rendered very distinct.

readily upon cold substances, and are not dissolved by water. But if a cold body, such as a porcelain dish (which answers the purpose best), is now depressed upon the flame, METALLIC ANTIMONY is deposited upon the surface in a state of the most minute division, forming a deep black and almost lustreless spot. If the middle part of the tube through which the gas is passing is heated to redness the bluish-green tint of the flame decreases in intensity, and a metallic mirror of antimony of silvery lustre is formed within the tube on both sides of the heated part.

As compounds of arsenic give under the same circumstances similar stains of metallic arsenic, it is always necessary to carefully examine the spots produced, in order to ascertain whether they really consist of antimony or contain any of that metal. With stains deposited on a porcelain dish the object in view is most readily attained by treating them with a solution of sodium hypochlorite (prepared by mixing a solution of "chloride of lime" with sodium carbonate in excess, and filtering), which will immediately dissolve arsenical stains, leaving those proceeding from antimony untouched, or, at least, removing them only after a very protracted action. A mirror within the glass tube, on the other hand, may be tested by heating it whilst the current of hydrogen gas still continues to pass through the tube; if the mirror volatilizes only at a higher temperature, and the hydrogen gas then issuing from the tube does not smell of garlic; if it is only with a strong current that the ignited gas deposits spots on porcelain, and the mirror before volatilizing fuses to small lustrous globules distinctly discernible through a magnifying glass,—the presence of antimony may be considered certain. Or the metals may be distinguished with great certainty by conducting through the tube a *very slow* stream of dry hydrogen sulphide, and heating the mirror, proceeding in an opposite direction to that of the current. The antimonial mirror is by this means converted into antimonious sulphide, which appears of a more or less reddish-yellow color, and almost black when in thick layers. If a feeble stream of dry hydrochloric acid gas is now transmitted through the glass tube, the antimonious sulphide, if present in thin layers only, disappears immediately; if the incrustation is somewhat thicker it takes a short time to dissipate it. The reason for this is, that the antimonious sulphide decomposes readily with hydrochloric acid, and the antimonious chloride formed is exceedingly volatile in a stream of hydrochloric acid gas. If the gaseous current is now conducted into some water the presence of antimony in the latter fluid may readily be proved by means of hydrogen sulphide. By this combination of reactions antimony may be distinguished with positive certainty from all other metals. The reaction which hydrogen gas containing antimonetted hydrogen shows with solution of silver nitrate and with solid potassa will be found in § 134, 6.

11. If a mixture of a compound of antimony with *sodium carbonate* and *potassium cyanide* is exposed on a charcoal support to the *reducing flame of the blowpipe*, brittle globules of METALLIC ANTIMONY are produced, which may be readily recognized by the peculiar reactions that mark their oxidation (compare § 131, 1).

12. In the upper reducing flame of the gas lamp (p. 30) compounds of antimony give a greenish-gray color, and no

odor. The *metallic incrustation* is black, sometimes dull, sometimes bright. The *incrustation of oxide* is white. When moistened with silver nitrate and then blown on with ammonia, it gives a black spot of argentous antimonate (BUNSEN).

§ 132.

d. ARSENIC, As. 75, and ARSENIOUS COMPOUNDS.

1. METALLIC ARSENIC has a blackish-gray color and high metallic lustre, which it retains in dry air, but loses in moist air ; the metallic arsenic of commerce is therefore commonly dull, with a dim bronze lustre on the planes of crystallization. Arsenic is not very hard, but very brittle : at a dull red heat it volatilizes without fusion. The fumes have a most characteristic odor of garlic. Heated with free access of air, arsenic burns—at an intense heat with a bluish flame—emitting white fumes of arsenious oxide, which condense on cold bodies. If arsenic is heated in a glass tube sealed at the lower end, the greater part of it volatilizes unoxidized, and recondenses above the heated spot as a lustrous black sublimate (arsenical mirror) ; a very thin coating of the sublimate appears of a brownish-black color. In contact with air and water arsenic oxidizes slowly to arsenious acid. Weak nitric acid converts it, with the aid of heat, into arsenious acid, which dissolves only sparingly in an excess of the acid ; strong nitric acid converts it partially into arsenic acid. It is insoluble in hydrochloric acid and dilute sulphuric acid ; concentrated boiling sulphuric acid oxidizes it to arsenious oxide, with evolution of sulphur dioxide.

2. ARSENIOUS OXIDE, As_2O_3, generally presents the appearance either of a transparent vitreous or of a white porcelain-like mass. By trituration it gives a heavy, white, gritty powder. When heated it volatilizes in white inodorous fumes. If the operation is conducted in a glass tube a sublimate is obtained consisting of small brilliant octahedrons and tetrahedrons. Arsenious oxide is only difficultly moistened by water ; it comports itself in this respect like a fatty substance. It is sparingly soluble in cold, but more readily in hot water. The solution is assumed to contain *arsenious acid*, $As(OH)_3$. This hydroxide, however, is not known to exist separately. It is copiously dissolved by hydrochloric acid, as well as by solution of soda and potassa. Upon boiling with nitro-hydrochloric acid it dissolves to arsenic acid. It is highly poisonous.

3. The ARSENITES are mostly decomposed upon ignition either into arsenates and metallic arsenic, which volatilizes, or into arsenious oxide and the base with which it was combined. Of the arsenites those only with alkali bases

are soluble in water. The insoluble arsenites are dissolved, or at least decomposed, by hydrochloric acid. Anhydrous ARSENIOUS CHLORIDE ($AsCl_3$) is a colorless volatile liquid, fuming in the air, which will bear the addition of a little water, but is decomposed by a larger amount into arsenious oxide, which partly separates, and hydrochloric acid, which retains the rest of the arsenious oxide in solution.

If a solution of arsenious oxide in hydrochloric acid is evaporated by heat, arsenious chloride escapes along with the hydrochloric acid.

4. *Hydrogen sulphide* colors aqueous solutions of arsenious acid yellow, but produces no precipitate in them; it fails equally to precipitate aqueous solutions of normal alkali arsenites, but upon addition of a strong acid a bright yellow precipitate of ARSENIOUS SULPHIDE (As_2S_3) forms at once. The same precipitate forms in like manner in the hydrochloric acid solution of arsenites insoluble in water. Even a large excess of hydrochloric acid does not prevent complete precipitation. Alkaline solutions are not precipitated. The precipitate is readily and completely dissolved by alkalies, alkali carbonates and alkali hydrogen carbonates, and also by alkali sulphides; but it is nearly insoluble in hydrochloric acid, even though concentrated and boiling. Boiling nitric acid decomposes and dissolves the precipitate readily.

The deflagration of arsenious sulphide with sodium carbonate and nitrate gives rise to the formation of sodium arsenate and sulphate, both of which are soluble in water and in diluted alcohol.

If recently precipitated arsenious sulphide is digested with sulphurous acid and hydrogen potassium sulphite, the precipitate is dissolved; upon heating the solution to boiling the fluid turns turbid, owing to the separation of sulphur, which upon continued boiling is for the greater part redissolved. The fluid contains, after expulsion of the sulphur dioxide, potassium arsenite and potassium thiosulphate $2(As_2S_3) + 8(K_2SO_3) + 8SO_2 = 4(KAsO_2) + 6(K_2S_2O_3) + S_2 + 7SO_2$ (BUNSEN).

If a solution of arsenious sulphide in potassa is boiled with basic bismuth nitrate or bismuth hydroxide, bismuth trisulphide and potassium arsenite are produced.

5. *Ammonium sulphide* also causes the formation of ARSENIOUS SULPHIDE. In neutral and alkaline solutions, however, the arsenious sulphide does not precipitate, but remains dissolved as ammonium sulpharsenite $(NH_4)_3AsS_3$. From this solution arsenious sulphide precipitates immediately upon the addition of a free acid.

6. *Silver nitrate* leaves aqueous solutions of arsenious acid perfectly clear, or at least produces only a trifling yellowish-white turbidity in them; but if a little ammonia is added a yellow precipitate of SILVER ARSENITE ($Ag_3 As O_3$) separates. The same precipitate forms of course immediately upon the addition of silver nitrate to the solution of a normal arsenite. The precipitate dissolves readily in nitric acid as well as in ammonia, and is not insoluble in ammonium nitrate; if therefore a small quantity of the precipitate is dissolved in a large amount of nitric acid, and the latter is afterwards neutralized with ammonia, the precipitate does not make its appearance again, as it remains dissolved in the ammonium nitrate formed. If an ammoniacal solution of silver arsenite is heated to boiling, METALLIC SILVER separates, the arsenious acid being converted into arsenic acid.

7. *Cupric sulphate* produces under the same circumstances as the silver nitrate a yellowish-green precipitate of CUPRIC ARSENITE.

8. If to a solution of arsenious oxide in an excess of solution of soda or potassa, or to a solution of an alkali arsenite mixed with *potassa* or *soda*, a few drops of a dilute solution of *cupric sulphate* are added, a clear blue fluid is obtained, which upon boiling deposits a red precipitate of CUPROUS OXIDE, leaving potassium arsenate in solution. This reaction is exceedingly delicate, provided not too much of the cupric sulphate be used. Even should the red precipitate be so exceedingly minute as to escape detection on looking across the tube, yet it will always be discernible with great distinctness upon looking down the test-tube. Of course this reaction, although really of great importance in certain instances as a confirmatory proof of the presence of arsenious acid, and more particularly also a means of distinguishing that acid from arsenic acid, is yet entirely inapplicable for the direct detection of arsenic, since grape sugar and other organic substances produce cuprous oxide from cupric salts in the same manner.

9. If a solution of arsenious oxide mixed with hydrochloric acid is heated with a perfectly clean slip of *copper* or copper wire, an iron-gray metallic film is deposited on the copper, even in highly dilute solutions; when this film increases in thickness it peels off in black scales. If the coated copper, after washing off the free acid, is heated with solution of ammonia, the film peels off from the copper, and separates in form of minute spangles (REINSCH). These are not pure arsenic, but consist of COPPER ARSENIDE ($Cu_3 As_2$). If the substance, either simply dried or oxidized by ignition in a current of air (which is attended with escape of some arsenious acid), is heated in a current of hydrogen, there escapes relatively but little arsenic, alloys richer in copper being left behind (FRESENIUS, LIPPERT). It is only after the presence of arsenic in the alloy has been fully demonstrated that this reaction can be considered a decisive proof of the presence of that metal, as antimony and other metals will under the same circumstances also precipitate in a similar manner upon copper.

10. If an acid or neutral solution of arsenious acid or any of its compounds

is mixed with *zinc*, *water*, and *dilute sulphuric acid*, ARSENETTED HYDROGEN ($As H_3$)* is formed, in the same manner as compounds of antimony give under

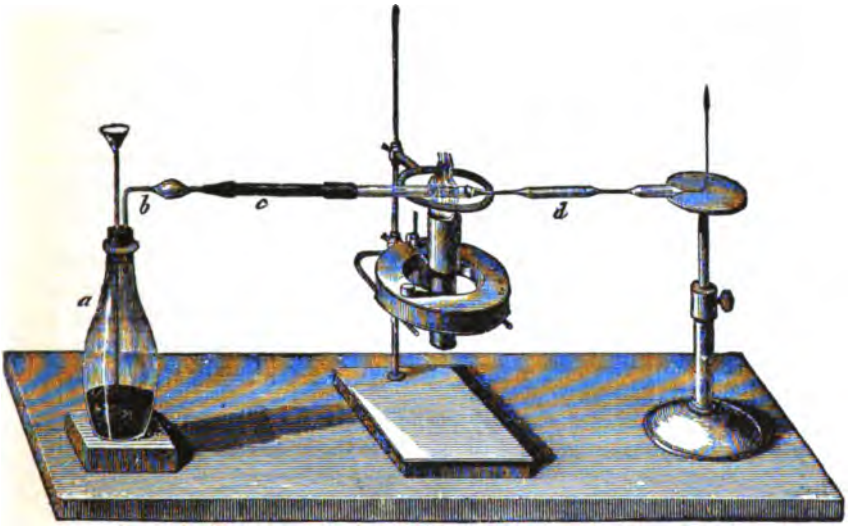


FIG. 36.

analogous circumstances antimonetted hydrogen. (Compare § 131, 10.) This reaction affords us a most delicate test for the detection of even the most minute quantities of arsenic. The operation is conducted in the apparatus illustrated by Fig. 36, or in one of similar construction.† *a* is the evolution flask, *b* a bulb intended to receive the water carried with the gaseous current, *c* a tube filled with cotton wool and small lumps of calcium chloride for drying the gas. This tube is connected with *b* and *d* by india-rubber tubes which have been boiled in solution of soda; *d* should have an inner diameter of 7 mm. (Fig. 37), and must be made of difficultly fusible glass free from lead. In experiments requiring great accuracy the tube should be drawn out as shown in Fig. 36. The operation is now commenced by evolving in *a* a moderate and uniform current of hydrogen gas, from pure granulated zinc, alloyed with a little platinum,‡ and pure sulphuric acid diluted with 3 to 4 times its bulk of water. When the evolution of hydrogen has proceeded for some time, so that it may safely be concluded the air has been completely expelled from the apparatus, the gas is kindled at the open end of the tube *d*. It is advisable to wrap a towel round the flask before kindling the gas, to guard against accidents in case of an explosion. It is now absolutely necessary first to ascertain whether the zinc and the sulphuric acid are quite free from any admixture of arsenic.

FIG. 37.

* [This gas is a deadly poison, and the utmost care should be taken not to inhale it or smell at the point of delivery. No harm can be experienced if the issuing gas be kept inflamed.—ED.]

† In toxical examinations the apparatus and procedure described in the 2d American edition of Fresenius' Quantitative Analysis, pp. 781–785, should be employed.

‡ For this purpose add 10 drops of hydrochloroplatinic acid solution to 100 grams of zinc; fuse and intermix in a porcelain dish and granulate by pouring into cold water.

This is done by depressing a porcelain dish horizontally upon the flame to make it spread over the surface : if the hydrogen contains arsenetted hydrogen, brownish or brownish-black stains of arsenic will appear on the porcelain ; the non-appearance of such stains may be considered as a proof of the freedom of the zinc and sulphuric acid from arsenic. In very accurate experiments, however, additional evidence is required to insure the positive certainty of the purity of the reagents employed ; for this purpose the part of the tube *d* shown in Fig. 36 over the flame is heated to redness with a Berzelius or gas lamp, and kept for fifteen minutes in a state of ignition : if no arsenical coating makes its appearance in the narrowed part of the tube the agents employed may be pronounced free from arsenic,* and the operation proceeded with, by pouring the fluid to be tested for arsenic through the funnel tube into the flask, and afterwards some water to rinse the tube. *Only a very little of the fluid ought to be poured in at first*, as in cases where the quantity of arsenic present is considerable, and a somewhat large supply of the fluid is poured into the flask, the evolution of gas often proceeds with such violence as to stop the further progress of the experiment. The remainder of the arsenical solution should be added *gradually in small portions at a time.*

Now if the fluid contains an oxygen or halogen compound of arsenic, there is immediately evolved, along with the hydrogen, arsenetted hydrogen, which at once imparts a bluish tint to the flame of the kindled gas, owing to the combustion of the particles of arsenic separating from the arsenetted hydrogen. At the same time white fumes of arsenious oxide arise, which condense upon cold objects. If a porcelain plate is now depressed upon the flame the separated and not yet reoxidized arsenic condenses upon the plate in black stains in a similar manner to antimony. (See § 131, 10.) The stains formed by arsenic incline, however, more to a blackish-brown tint, and show a bright metallic lustre; whilst the antimonial stains are of a deep black color and but feebly lustrous. The arsenical stains may be distinguished, moreover, from the antimonial stains by solution of sodium hypochlorite (compare § 131, 10), which will at once dissolve arsenical stains, leaving antimonial stains unaffected, or removing them only after a considerable time.

If the heat of a Berzelius or gas lamp is now applied to the part of the tube *d*, shown in Fig. 36 over the flame, a brilliant arsenical mirror makes its appearance in the narrowed portion of the tube behind the heated part; this mirror is of a darker and less silvery-white hue than that produced by antimony under similar circumstances; from which it is, moreover, distinguished by the facility with which it may be dissipated in a current of hydrogen gas without previous fusion, and by the characteristic odor of garlic emitted by the escaping (unkindled) gas. If the gas is kindled whilst the mirror in the tube is being heated, the flame will, even with a very slight current of gas, deposit arsenical stains on a porcelain plate.

The reactions and properties just described are amply sufficient to enable us to distinguish between arsenical and antimonial stains and mirrors; but they will often fail to detect arsenic with positive certainty in presence of antimony. In cases of this kind the following process will serve to set at rest all possible doubt as to the presence or absence of arsenic:

* In judicial cases this testing of the reagents should occupy 2 to 3 hours, and should consume as much zinc and other reagents as are required in obtaining *all* the arsenic from say 100 grams of suspected matters. (See Fres. Quant., pp. 781-785).

Heat the long tube, through which the gas to be tested is passing, to redness in several parts, to produce distinct metallic mirrors; then transmit through the tube a very weak stream of dry hydrogen sulphide, and heat the metallic mirrors proceeding from the outer towards the inner border. If arsenic alone is present yellow arsenious sulphide is formed inside the tube; if antimony alone is present an orange-red or black antimonious sulphide is produced; and if the mirror consisted of both metals the two sulphides appear side by side, the arsenious sulphide, as the more volatile, lying invariably before the antimonious sulphide. If you now transmit through the tube containing either sulphide, or both sulphides together, dry hydrochloric gas, without applying heat, no alteration will take place if arsenious sulphide alone is present, even though the gas be transmitted through the tube for a considerable time. If antimonious sulphide alone is present this will entirely disappear, as already stated (§ 131, 10), and if both sulphides are present, the antimonious sulphide will immediately volatilize, whilst the yellow arsenious sulphide will remain. If a small quantity of ammonia is now drawn into the tube, the arsenious sulphide is dissolved, and may thus be readily distinguished from sulphur which may have separated. My personal experience has convinced me of the infallibility of these combined tests for the detection of arsenic.

The reaction of hydrogen containing arsenetted hydrogen with solution of silver nitrate will be found in § 134, 6.

MARSH was the first who suggested the method of detecting arsenic by the production of arsenetted hydrogen.

[11. When to a solution of arsenious chloride or of arsenious oxide, or of an arsenite in *fuming hydrochloric acid*, crystals or highly concentrated solutions

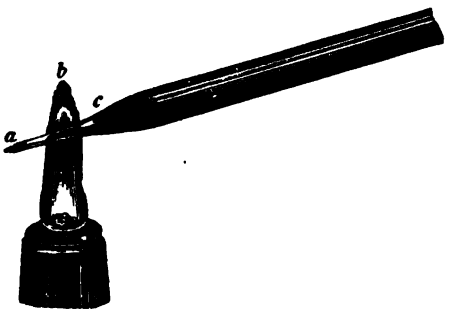


FIG. 88.

of *stannous chloride* are added, and the still fuming mixture boiled, all the arsenic present separates in dark-brown crystalline flocks of an ALLOY OF ARSENIC AND TIN (containing 8 to 6 per cent. of tin). In dilute hydrochloric acid (with less than 20 per cent. H Cl) the precipitation is incomplete or does not occur at all. The precipitate after settling may be washed, first with hydrochloric acid, sp. gr. 1.1, then with water or alcohol, and dried at a gentle warmth. A portion of it is then heated in a tube like that shown in Fig. 88, to procure the arsenical mirror.

In liquids containing very minute traces of arsenic, the precipitate remains

a long time suspended in the liquid, giving it a brownish color. This color distinctly appears in solutions containing but $\frac{1}{1000000}$ of arsenic. Antimony is not thrown down by stannous chloride under any circumstances whatever.—BETTENDORF.]

12. If a small lump of arsenious oxide (*a*) be introduced into the pointed end of the drawn-out glass tube (Fig. 38), a fragment of quite recently ignited charcoal (*b*) pushed down the tube to within a short distance of the arsenious oxide, and first the charcoal then the arsenious oxide heated to redness, a MIRROR OF METALLIC ARSENIC will form at *c*, owing to the reduction of the arsenious oxide vapor by the red-hot charcoal. If the tube be now cut between *b* and *c* and then heated in an inclined position, with the cut end *c* turned upwards, the metallic mirror will volatilize, emitting the characteristic odor of garlic. This is both the simplest and safest way of detecting pure arsenious oxide.

13. If arsenites, or arsenious oxide, or arsenious sulphide are fused with a mixture of equal parts of dry *sodium carbonate* and *potassium cyanide*, the whole of the arsenic is reduced to the metallic state,* and so is the base also, if easily reducible; the eliminated oxygen converting part of the potassium cyanide into potassium cyanate. In the reduction of arsenious sulphide potassium sulphocyanate is formed. The operation is conducted as follows: Introduce the perfectly dry arsenical compound into the bulb of a small bulb-tube (Fig. 39), and cover it with six times the quantity of a perfectly dry mixture of equal parts of sodium carbonate and of potassium cyanide. The whole quantity must not much more than half fill the bulb, otherwise the fusing potassium

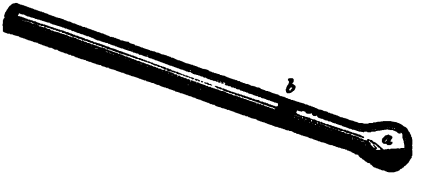


FIG. 39.

cyanide is likely to ascend into the tube. Heat the bulb gently; should some water still escape, wipe the inside of the tube perfectly dry with a twisted slip of blotting-paper. It is of the highest importance for the success of the experiment to bestow great care upon expelling the water, drying the mixture, and wiping the tube clean and dry. Apply now a strong heat to the bulb, to effect the reduction of the arsenical compound, and continue this for some time, as the arsenic often requires some time for its complete sublimation. The mirror which is deposited at *b* is of exceeding purity. It is obtained from all arsenites whose bases remain either altogether unaffected, or are reduced to such metallic arsenides as lose their arsenic partly or totally upon the simple application of heat. This method deserves to be particularly recommended, even in cases where only minute quantities of arsenic are present. For the direct production of arsenic from arsenious sulphide it is superior to all other methods.

* [According to Rose and Mohr, the reduction of the arsenic is never complete, and when excess of sulphur is mixed with the $As_2 S_3$, no metallic arsenic whatever can be made to appear.—Ed.]

The delicacy of the reaction is heightened by heating the mixture in a stream of dry carbon dioxide. The most accurate and satisfactory results are obtained in the following manner. Figs. 40 and 41 show the apparatus in which the process is conducted.

The self-regulating gas-generating apparatus is like that already described for preparing hydrogen sulphide (see § 84, Fig. 35), but is charged with lumps of marble, and the delivery tube passes a cork in the mouth of a flask containing oil of vitriol, in order to dry the gas, whence it streams through the reduction tube, which should have an inner diameter of about three-eighths of an inch. This tube is represented of one-third its proper size, in Fig. 41.

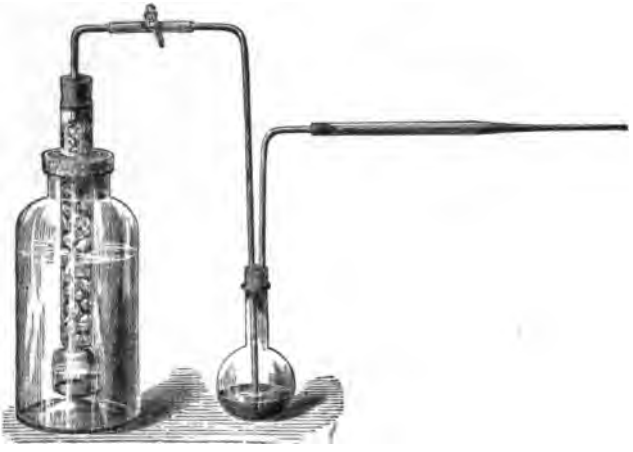


FIG. 40.

When the apparatus is full of carbon dioxide, triturate the perfectly dry arsenious sulphide or arsenite in a slightly heated mortar with about twelve parts of a well-dried mixture consisting of three parts of sodium carbonate and one part of potassium cyanide. The mixture must of course be quite free from arsenic (§ 46). Put the powder upon a narrow slip of paper, bent into the shape of a gutter, and push this into the reduction tube down to *e*; turn the tube now half way round its axis, when the mixture will drop into the tube between *e* and *d*, every other part remaining perfectly clean. Connect the tube now with the gas apparatus, and pass through it a moderate stream of carbon dioxide. Heat the tube in its whole length very gently until the mixture in it is quite dry. When every trace of water is expelled, reduce the gas stream so that the single bubbles pass through the sulphuric acid at intervals

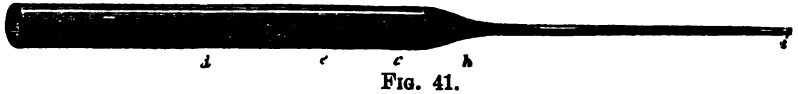


FIG. 41.

of one second, and heat the reduction tube to redness at *c* (Fig. 41). When *c* is red hot, apply the flame of a second lamp to the mixture, proceeding from

d to *e*, until the whole of the arsenic is expelled. The far greater portion of the volatilized arsenic recondenses at *h*, whilst a small portion only escapes through *i*, imparting to the air a garlic odor. Advance the flame of the second lamp slowly and gradually up to *c*, by which means the whole of the arsenic which may have condensed in the wide part of the tube is driven to *h*. When you have effected this, close the tube at the point *i* by fusion, and apply heat, proceeding from *i* towards *h*, by which means the extent of the mirror is narrowed, whilst its beauty and lustre are correspondingly increased. In this manner perfectly distinct mirrors of arsenic may be produced from .0002 grm. of arsenious sulphide. No mirrors are obtained by this process from antimonious sulphide, or from any other compound of antimony.

14. If arsenious oxide or an arsenite is exposed on charcoal to the reducing *flame of the blowpipe* a highly characteristic garlic color is emitted, more especially if some sodium carbonate is added. This odor has its origin in the reduction and reoxidation of the arsenic, and enables us to detect very minute quantities. This test, however, like all others that are based upon the indications of the sense of smell, cannot be implicitly relied on.

§ 133.

e. Arsenic Compounds, As. 75.

1. Orthoarsenic acid crystallizes in prisms or plates of the formula $As O_4H_3 . \frac{1}{2} H_2O$ or $As O (O H)_3 . \frac{1}{2} H_2 O$, which deliquesce in the air. The water of crystallization escapes at 100°; at 180° under loss of water, it is converted into pyroarsenic acid ($As_2 O_7 H_4$), at 206° it passes into metarsenic acid ($As O_3 H$). Heated to faint redness these hydroxides leave arsenic oxide ($As_2 O_5$). This again on strong ignition splits into oxygen and arsenious oxide. Arsenic oxide dissolves but slowly in water. The meta- and pyroarsenic acids dissolve in water to orthoarsenic acid, and the meta- and pyroarsenates which are soluble dissolve at once as orthoarsenates. Arsenic acid is poisonous.

2. Most of the arsenates are insoluble in water. Of the orthoarsenates those with alkali bases alone are soluble in water. Most of the di- and trimetallic arsenates can bear a strong red heat without suffering decomposition. The monometallic orthoarsenates lose acid upon ignition, which passes off in the form of arsenious oxide and oxygen. A solution of arsenic acid or of an arsenate in hydrochloric acid may be boiled for a long time without losing arsenic, provided too much hydrochloric acid is not present. But when the residual fluid contains about half its volume of hydrochloric acid of specific gravity 1.12, traces of arsenious chloride begin to escape with the hydrochloric acid.

3. *Hydrogen sulphide* fails to precipitate alkaline and neutral solutions; but in acidified solutions it causes first reduc-

tion of the arsenic acid to arsenious acid, with separation of sulphur, then precipitation of arsenious sulphide. This process continues until the whole of the arsenic is thrown down as $As_2 S_3$, mixed with 2 S (WACKENRODER, LUDWIG, H. ROSE). The action never takes place immediately, and in dilute solutions frequently only after the lapse of a considerable time (twelve to twenty-four hours, for instance). Heating (to about 70°) greatly accelerates the action. If a solution of arsenic acid, or of an arsenate, is mixed with sulphurous acid, or with sodium sulphite and some hydrochloric acid, the sulphurous acid is converted into sulphuric acid, and the arsenic acid reduced to arsenious acid; application of heat promotes the change. If hydrogen sulphide is now added, the whole of the arsenic is immediately thrown down as arsenious sulphide.

4. *Ammonium sulphide*, especially upon boiling and evaporating therewith, converts the arsenic acid in neutral and alkaline solutions of arsenates into ARSENIC SULPHIDE ($As_2 S_5$), which remains in solution as ammonium sulpharsenate $(N H_4)_3 As S_4$. Upon the addition of an acid to the solution this salt is decomposed, and arsenic sulphide precipitates. The separation of this precipitate proceeds more rapidly than is the case when acid solutions of arsenates are precipitated with hydrogen sulphide. It is promoted by heat. The precipitate formed is $As_2 S_5$, and not a mixture of $As_2 S_3$ with S_2.

5. *Silver nitrate* produces, under the circumstances stated § 132, 6, a highly characteristic reddish-brown precipitate of SILVER ARSENATE ($Ag_3 As O_4$), which is readily soluble in dilute nitric acid and in ammonia, and dissolves also slightly in ammonium nitrate. Accordingly, if a little of the precipitate is dissolved in a large proportion of nitric acid, neutralization with ammonia often fails to produce the precipitate. The ammoniacal solution of silver arsenate does not deposit silver upon boiling (difference between arsenic and arsenious acids).

6. *Cupric sulphate* produces, under the circumstances stated § 132, 7, a greenish-blue precipitate of HYDROGEN CUPRIC ARSENATE ($H Cu As O_4$).

7. If a dilute solution of arsenic acid mixed with some hydrochloric acid is heated with a clean slip of *copper* the metal remains perfectly clean (WERTHER, REINSCH); but if to one volume of the solution two volumes of concentrated hydrochloric acid are added, a gray film is deposited on the copper, as in the

case of arsenious acid. The reaction is under these circumstances equally delicate as with arsenious acid (REINSCH).

8. With *zinc* in presence of sulphuric acid, with *stannous chloride*, with *potassium cyanide*, and before the *blowpipe*, the compounds of arsenic acid comport themselves in the same way as those of arsenious acid. If the reduction of arsenic acid by zinc is effected in a platinum capsule, the platinum does not turn black (difference from antimony).

9. If a solution of arsenic acid, or of an arsenate soluble in water, is added to a clear mixture of *magnesium sulphate*, *ammonium chloride*, and a sufficient quantity of *ammonia*,* a crystalline precipitate of AMMONIUM MAGNESIUM ARSENATE ($NH_4MgAsO_4.6H_2O$) separates; from concentrated solutions immediately, from dilute solutions after some time. If a small portion of the precipitate is dissolved on a watch-glass in a drop of nitric acid, a little silver nitrate added, and the solution touched with a glass rod dipped in ammonia, brownish-red silver arsenate is formed. Or if a small portion of the precipitate is dissolved in hydrochloric acid and hydrogen sulphide is passed into the solution with warming, a yellow precipitate is formed. (Differences between ammonium magnesium arsenate and phosphate.)

§ 134.

Recapitulation and remarks.—I will here describe first the different ways adapted to effect the detection or separation of tin, antimony and arsenic, when present together, and afterwards the means of distinguishing between the several oxides and acids of the three metals.

1. If you have a mixture of sulphides of tin, antimony and arsenic, triturate 1 part of it with 1 part of dry sodium carbonate and 1 part of sodium nitrate, and transfer the mixed powder gradually to a small porcelain crucible containing 2 parts of sodium nitrate kept in a state of fusion at a not overstrong heat; oxidization of the sulphides ensues, attended with slight deflagration. The fused mass contains stannic oxide, sodium arsenate and metantimonate, with sodium sulphate, carbonate, nitrate and nitrite. You must take care not to raise the heat to such a degree, nor continue the fusion so

* The "magnesia mixture" is prepared by dissolving together 1 part of crystallized magnesium sulphate and 2 parts of pure ammonium chloride in 8 parts of water, adding 4 parts solution of ammonia, and filtering after standing some days.

long, as to lead to decomposition of the sodium nitrite, with formation of sodium stannate soluble in water. Upon treating the mass with a little cold water, stannic oxide and sodium metantimonate remain undissolved, whilst sodium arsenate and the other salts are dissolved. If the filtrate is acidified with nitric acid, and heat is applied to remove carbonic and nitrous acids, the ARSENIC ACID may be detected and separated, either with silver nitrate, according to § 133, 5, or with a mixture of magnesium sulphate, ammonium chloride, and ammonia, according to § 133, 9.

If the undissolved residue, consisting of stannic oxide and sodium metantimonate is, after being washed once with cold water and three times with dilute alcohol, digested with strong hydrochloric acid at a gentle heat for some time, the mass is either completely dissolved or, if the tin is present in a large proportion, a white residue is left undissolved. If now the free acid is mostly removed by evaporation, some water, a fragment of zinc and a bit of platinum foil (the two metals in contact) be added, the compounds are reduced to the metallic state,* when the ANTIMONY will at once reveal its presence by blackening the platinum. If, after the evolution of hydrogen has nearly stopped, the remainder of the zinc is taken away, any adhering tin being rubbed off and left in the vessel, and the contents of the dish are heated with some hydrochloric acid, the reduced TIN dissolves to stannous chloride, whilst the antimony is left undissolved in the form of black flakes. The tin may then be more distinctly tested in the solution, with mercuric chloride, or with a mixture of ferric chloride and potassium ferricyanide, and the antimony, after solution in a little aqua regia, with hydrogen sulphide. As this method of detecting arsenic, tin and antimony, in presence of each other is adopted in the systematic course of analysis, I have here simply explained the principle upon which it is based, and refer for the details of the process to § 185.

2. If the mixed sulphides, after being freed from the greater part of the adhering water, by laying the filter containing them on blotting paper, are treated with fuming hydrochloric acid, with application of a gentle heat, the sulphides of antimony and tin dissolve, whilst the arsenious sulphide is left almost completely undissolved. By treating this with ammonia and evaporat-

* Except a portion of stannic oxide that was undissolved.

ing the solution obtained, with addition of a small quantity of sodium carbonate, an arsenical mirror may easily be produced from the residue, by means of potassium cyanide and sodium carbonate in a stream of carbonic acid gas (§ 132, 13). The solution, which contains the tin and the antimony, may be treated as stated in 1.

If a great excess of antimony is present, the latter solution may also be mixed with the transparent portion of commercial "carbonate of ammonia," in excess, and boiled, when a large proportion of the antimony will dissolve, leaving stannic oxide behind, mixed with but little antimonious oxide, in which undissolved residue the tin may now be the more readily detected by the method described in 1 (BLOXAM).

3. If the mixed sulphides are digested at a gentle heat with some solid ammonium carbonate and water, arsenious sulphide dissolves, whilst the antimony and tin sulphides remain undissolved. But this separation is not quite absolute, as traces of antimony are apt to pass into the solution, whilst some arsenious sulphide remains in the residue. The arsenious sulphide precipitating from the alkaline solution upon acidifying this latter with hydrochloric acid must, therefore, especially if consisting only of a few flakes, after washing, be treated with ammonia, the solution evaporated, with addition of a small quantity of sodium carbonate, and the residue fused with potassium cyanide in a stream of carbon dioxide, to make quite sure by the production of an arsenical mirror. The residue, insoluble in ammonium carbonate, should be treated as directed in 2.

4. If the sulphides of antimony, tin and arsenic are dissolved in potassium sulphide, a *large* excess of a concentrated solution of sulphurous acid added, the mixture digested for some time on the water-bath, boiled until all sulphurous acid is expelled, then filtered, the filtrate contains all the arsenic as arsenious acid (which may be precipitated from it by hydrogen sulphide), whilst antimonious sulphide and stannic sulphide are left behind undissolved (BUNSEN). These latter may then be treated as directed in 2.

5. In the analysis of alloys, metastannic acid, antimonious oxide, and arsenic acid are often obtained together as a residue insoluble in nitric acid. The best way is to fuse this residue with sodium hydroxide in a silver crucible, to treat the mass with water, and add one-third (by volume) of alcohol; then to filter the fluid off from the sodium pyroantimonate, which remains undissolved, and wash the latter with alcohol mixed with a few drops of solution of sodium carbonate. In the presence of much tin it is advisable to repeat the above treatment on the residue, in order to extract all the tin. The filtrate is acidified with hydrochloric acid, and the tin and arsenic are then precipitated as sulphides, with the aid of heat. On heating the precipitated sulphides in a stream of hydrogen sulphide the whole of the tin is left as sulphide, whilst the arsenious sulphide volatilizes, and may be received in solution of ammonia (H. ROSE).

6. For the method of separating antimony and arsenic, and distinguishing between the two metals, by treating the mirror produced by MARSH'S process, with hydrogen sulphide, and separating the resulting sulphides by means of hydrochloric acid gas, I refer to § 132, 10. Antimony and arsenic may, however, when mixed together in form of hydrogen compounds, be separated also in the following ways : *a.* Conduct the gases mixed with an excess of hydrogen, first through a tube containing glass splinters moistened with solution of lead acetate to retain the hydrochloric and hydrosulphuric gases, then in a

slow stream into a solution of silver nitrate. Almost all the antimony in the gas falls down as black silver antimonide (Ag_3Sb), whilst the arsenic passes into the solution as arsenious acid, with reduction of the silver, and may be detected in the fluid as silver arsenite, by cautious addition of ammonia, or—after precipitating the excess of silver by hydrochloric acid—by means of hydrogen sulphide. Since, however, a little antimony always passes into the solution, the precipitate by hydrogen sulphide must not be put down as arsenious sulphide without further examination, according to § 132, 13. In the precipitated silver antimonide, which is often mixed with much silver, the antimony may be most readily detected, by heating the precipitate—thoroughly freed from arsenious acid by boiling with water—with tartaric acid and water to boiling. This will dissolve the antimony alone, which may then be readily detected by means of hydrogen sulphide in the solution acidified with hydrochloric acid (A. W. HOFMANN). *b.* Conduct the gases mixed with an excess of hydrogen through a rather wide glass tube, 3 or 4 inches of which are filled with caustic potassa in small lumps. The potassa decomposes the antimonetted hydrogen entirely, becoming coated with a lustrous film of metal. The arsenetted hydrogen is on the contrary not decomposed, and may be detected readily on its exit from the tube by the production of the arsenical mirror (§ 132, 10), or by its action on solution of silver nitrate (DRAGENDORFF).

7. *Stannous and stannic compounds* may be detected in presence of each other, by testing one portion of the solution for the first with mercuric chloride, hydrochlorauric acid or a mixture of potassium ferricyanide and ferric chloride, and another portion for stannic compounds, by pouring it into a concentrated hot solution of sodium sulphate. For the last test the solution must not contain much free acid.

8. *Antimonious oxide* in presence of *antimonic acid* may be identified by the reaction described in § 131, 9. *Antimonic acid* in presence of *antimonious oxide*, by heating the oxide, which must be free from other bodies, with hydrochloric acid and potassium iodide (§ 131, 2 and 3).

9. *Arsenious acid* and *arsenic acid* in the same solution may be distinguished by means of silver nitrate. If the precipitate contains little arsenate and much arsenite of silver it is necessary, in order to identify the former, to add cautiously and drop by drop most highly dilute nitric acid, which dissolves the yellow silver arsenite first. A still safer way to detect small quantities of arsenic acid in presence of arsenious acid is to precipitate the solution with a mixture of magnesium sulphate, ammonium chloride, and ammonia (§ 132, 9), by which means an actual separation of the two acids is effected.

Arsenious acid may be recognized in presence of arsenic acid by the imme-

diate precipitation of the acidified solution with hydrogen sulphide in the cold; also by the reduction of cupric oxide in alkaline solution; also by the separation of metallic silver by boiling the ammoniacal solution of the silver salts.

To ascertain the degree of sulphuration of arsenic in a sulphur salt, boil the alkaline solution of the salt under examination with bismuth hydroxide, filter off from the bismuth trisulphide formed, and test the filtrate for arsenious and arsenic acids. To distinguish between the arsenious and arsenic sulphides, extract first the sulphur which may be present, by means of carbon disulphide, then dissolve the residue in ammonia, add silver nitrate in excess, filter off the silver sulphide, and observe whether arsenite or arsenate of silver is formed upon addition of ammonia.

Special Reactions of the rarer Metals of the Sixth Group.

§ 135.

a. Iridium, Ir. 198.

Iridium is found in combination with platinum and other metals in platinum ores; also, and more especially, as a native alloy of osmium and iridium. Alloyed with platinum, it has of late been employed for crucibles, etc. Iridium resembles platinum, but it is brittle; it fuses with extreme difficulty. In the compact state, or reduced at a red heat by hydrogen, it dissolves in no acid, not even in aqua regia (difference between iridium and gold and platinum); reduced in the moist way, say by formic acid, or largely alloyed with platinum, it dissolves in aqua regia to tetrachloride. *Potassium disulphate* in a state of fusion will oxidize but not dissolve it (difference between iridium and rhodium). It oxidizes by fusion with *sodium hydroxide* with access of air, or by fusion with sodium nitrate. The sodium periridiate which is formed in this process dissolves partially in water; by heating with aqua regia it gives a deep black-red solution of iridic sodium chloride, $IrCl_4.2\,NaCl$.

If iridium powder is mixed with sodium chloride, the mixture heated to incipient redness, and treated with *chlorine gas*, iridic sodium chloride is formed, which dissolves in water to a deep red-brown fluid. *Potassa*, added in excess, colors the solutions greenish, a little brownish-black iridic potassium chloride precipitating at the same time. If the solution is heated, and exposed some time to the air, it acquires at first a reddish tint, which changes afterwards to azure blue (characteristic difference between iridium and platinum); if the solution is now evaporated to dryness, and the residue treated with water, a colorless fluid is obtained, with a blue deposit of iridic hydroxide, $Ir(OH)_4$, left undissolved. *Hydrogen sulphide* in the first place decolorizes solutions of iridic tetrachloride, iridious chloride, Ir_2Cl_6, is formed, with separation of sulphur, and finally brown iridium sulphide precipitates. *Ammonium sulphide* produces the same precipitate, which redissolves readily in an excess of the precipitant. *Potassium chloride* precipitates iridic potassium chloride as a dark-brown powder, insoluble in a concentrated solution of potassium chloride. *Ammonium chloride* precipitates from concentrated solutions iridic ammonium chloride in the form of a dark-red powder, consisting of microscopic octahedrons, insoluble in concentrated solution of ammonium chloride.

This double salt (and also the corresponding potassium compound), especially when in hot solution, is turned olive-green by *potassium nitrite*, owing to the formation of iridious potassium chloride $Ir_2 Cl_6 . 6 K Cl . 6 H_2 O$; this double salt crystallizes out on cooling. On heating or evaporating the green solution with an excess of potassium nitrite, it turns yellow, and when boiled deposits a white precipitate which is hardly soluble in water and hydrochloric acid. (This reaction may be taken advantage of to separate iridium from platinum.—GIBBS.) If the iridic ammonium chloride is dissolved in water by boiling, and *oxalic acid* is added, a reduction to the iridious salt takes place, and on this account the solution remains clear on cooling (here iridium differs from platinum.—C. LEA). If *stannous chloride* is added to iridic chloride and the solution is boiled, and then excess of potassa is added and the mixture is boiled again, a leather-colored precipitate is formed. *Ferrous sulphate* decolorizes the solution, but does not produce a precipitate. *Zinc* precipitates black metallic iridium. On suspending iridic hydroxide in a solution of *potassium sulphite*, saturating with *sulphurous acid* and boiling with renewal of the evaporating water till all the free sulphurous acid is expelled, the whole of the iridium is converted into insoluble iridic sulphite (any platinum which may be present will remain dissolved as platinous potassium sulphite.—C. BIRNBAUM). Ignited with *sodium carbonate* in the upper oxidizing flame, compounds of iridium yield the metal, which when washed out is gray, devoid of lustre, and without ductility.

b. MOLYBDENUM, Mo. 96.

MOLYBDENUM is not largely disseminated in nature, and is found only in moderate quantities, more especially as molybdic sulphide, $Mo S_2$, and as lead molybdate (yellow lead ore). Since the use of ammonium molybdate as a means of detecting and determining phosphoric acid, molybdenum has acquired considerable importance in practical chemistry. MOLYBDENUM is tin-white and hard; when heated in the air it oxidizes; it is soluble in nitric acid and very difficult to fuse. The MONOXIDE is black, the DIOXIDE is dark-brown. When heated in the air or treated with nitric acid, the metal and oxides are all converted into TRIOXIDE or molybdic anhydride, $Mo O_3$. The trioxide is a white porous mass, which in water separates into fine scales, and dissolves to a slight extent as molybdic acid; it fuses at a red heat; in close vessels it volatilizes only at a very high temperature, in the air it volatilizes easily at a red heat and sublimes to transparent laminæ and needles. On igniting it in a current of hydrogen, it is first converted into the dioxide, and afterwards by strong and long-continued heating into the metal. The non-ignited trioxide dissolves in acids. The solutions are colorless; the hydrochloric solution is colored by contact with zinc soon, on addition of stannous chloride immediately, the color being brown, green or blue according to the proportion of reducing agent and the concentration of the fluid. Digested with *copper* the sulphuric acid solution turns blue, the hydrochloric acid solution brown. The reaction often requires some time. [Molybdic acid heated with a few drops of *strong sulphuric acid* on platinum foil until copious fumes are evolved, is converted into molybdous sulphate, and when the mass is allowed to cool, and is then breathed upon, it acquires an ultramarine blue color (distinction from Ti, W, and V.—SCHÖNN, MASCHKE). ED.] *Potassium ferrocyanide* produces a reddish-brown precipitate, *infusion of galls* a green precipitate. *Hydrogen sulphide*, added

in small proportion, imparts a blue tint to the solutions of trioxide; added in larger proportion, it produces a brownish-black precipitate; the fluid over the latter at first appears green, but after being allowed to stand for some time, and heated, additional quantities of hydrosulphuric acid being repeatedly conducted into it, the whole of the molybdenum present will ultimately, though slowly, separate as brownish-black molybdenum trisulphide, MoS_3. The precipitated molybdenum trisulphide dissolves in sulphides of the alkali metals; acids precipitate from the sulphomolybdates thus formed molybdenum trisulphide again; application of heat promotes the separation. By heating to redness in the air, or by heating with nitric acid, molybdenum sulphides are converted into trioxide. If a solution of trioxide in excess of ammonia (*i.e.* ammonium molybdate) is mixed with yellow ammonium sulphide, and boiled for some time, a dark-red liquid of great depth of color is formed in addition to the brownish-black precipitate, unless a very large excess of ammonium sulphide is present. Potassium sulphocyanate, if added to a solution of trioxide or of a molybdate containing hydrochloric acid, produces no color until zinc is added, when the fluid becomes crimson; the coloration is due to the formation of a sulphocyanate of molybdenum. Phosphoric acid does not destroy the color (difference from ferric sulphocyanate). On shaking the red fluid with ether, the latter becomes colored (C. D. BRAUN).

To recognize molybdenum in presence of ferric oxide and nitrogen tetroxide, which likewise give a red color with potassium sulphocyanate, the solution is treated with sulphurous acid or an alkali sulphite and hydrochloric acid until no coloration is produced in it by potassium sulphocyanate alone. Ferric oxide is thus reduced to ferrous oxide, and nitrogen tetroxide to a lower oxide. On now adding solution of potassium sulphocyanate and a fragment of zinc, the reaction at once becomes manifest.—(EDITOR.)

[Molybdic solutions acidified with dilute hydrochloric acid impart a brown tint to turmeric paper.—(A. MÜLLER.) (Compare zirconia and boric acid.) ED.]

Molybdenum trioxide dissolves readily in solutions of *alkalies* and *alkali carbonates;* from concentrated solutions *nitric acid* or *hydrochloric acid* throws down molybdic acid ($MoO_2(OH)_2$?), which redissolves in a large excess of the precipitant. The solutions of molybdates of the alkali metals are colored yellow by *hydrogen sulphide*, and give afterwards, upon addition of acids, a brownish-black precipitate. For the deportment of molybdic acid with *orthophosphoric acid* and ammonia, see § 142, 10.

Molybdenum trioxide volatilizes when heated on charcoal in the *oxidizing flame*, coating the charcoal with a yellow, often crystalline, powder, which turns white on cooling. In the *reducing flame* the acid suffers reduction to the metallic state; the molybdenum is obtained as a gray powder by elutriating the charcoal support. Molybdenum sulphide gives in the oxidizing flame sulphur dioxide and an incrustation of molybdenum trioxide on the charcoal.

c. TUNGSTEN, W. 184.

This metal most commonly occurs in nature in the forms of calcium tungstate and of the ferrous manganous tungstate called wolfram. Obtained by the reduction of tungstic oxide in a current of hydrogen at an intense red heat, it is an iron-gray powder very difficultly fusible. This powder is converted by ignition in the air into tungstic oxide (or anhydride) (WO_3); by

ignition in a current of dry air-free chlorine into dark violet hexachloride ($W Cl_6$) which sublimes, and the still more volatile red pentachloride. These chlorides are decomposed by water into the corresponding hydroxides and hydrochloric acid. Tungsten is insoluble or scarcely soluble in acids, even in aqua regia, and also in potassa; it dissolves, however, in the latter if mixed with sodium hypochlorite. TUNGSTEN DIOXIDE is brown; by intense ignition with free access of air it is converted into tungstic oxide (trioxide). TUNGSTIC OXIDE is lemon-yellow, fixed, insoluble in water and acids. By fusing tungstic oxide with potassium disulphate, and treating the fused mass with water, an acid solution is obtained, which contains no tungstic acid; after the removal of this solution the residue, consisting of potassium tungstate and a large excess of tungstic acid, completely dissolves in water containing ammonium carbonate (means of separating tungstic from silicic acid). Alkali tungstates soluble in water are formed readily by fusion with alkali carbonates, but with difficulty by boiling with solution of the same. *Hydrochloric acid, nitric acid,* and *sulphuric acid* produce in the solution of these tungstates white precipitates of tungstic acid ($W O (O H)_4$) which turn yellow ($W O_2 (O H)_2$) on boiling, and are insoluble in an excess of the acids (difference from molybdic acid), but soluble in ammonia. Upon evaporating with an excess of hydrochloric acid to dryness, and treating the residue with water, the tungstic acid is left undissolved. *Barium chloride, calcium chloride, lead acetate silver nitrate, mercurous nitrate* produce white precipitates. *Potassium ferrocyanide,* with addition of some acid, colors the fluid deep brownish-red, and after some time produces a precipitate of the same color. *Tincture of galls,* with a little acid added, produces a brown precipitate. *Hydrogen sulphide* barely precipitates acid solutions. *Ammonium sulphide* fails to precipitate solutions of alkali tungstates; upon acidifying the mixture light-brown trisulphide precipitates, which is slightly soluble in pure water, but insoluble in water containing salts. *Stannous chloride* produces a yellow precipitate; on acidifying with hydrochloric acid, and applying heat, this precipitate acquires a beautiful blue color (highly delicate and characteristic reaction). If solutions of alkali tungstates are mixed with hydrochloric acid, or better still, with an excess of phosphoric acid, and *zinc* is added, the fluid acquires a beautiful blue color. Fusing *sodium metaphosphate* dissolves tungstic oxide. The bead, exposed to the oxidizing flame, appears clear, varying from colorless to yellowish; in the reducing flame it acquires a pure blue color, and upon addition of ferrous oxide a blood-red color. By mixing with a little *sodium carbonate,* and exposing in the cavity of the charcoal support to the reducing flame, tungsten in powder is obtained, which may be separated by washing. The tungstates which are insoluble in water may, most of them, be decomposed by digestion with acids. Wolfram, which strongly resists the action of acid, is fused with alkali carbonate, when water will dissolve out of the fused mass the alkali tungstate formed.

d. TELLURIUM, Te. 128.

TELLURIUM is not widely disseminated, and is found in small quantities only in the native state, or alloyed with other metals, or as tellurous oxide. It is a white, brittle, but readily fusible metal, which may be sublimed in a glass tube. Heated in the air it burns with a greenish-blue flame, emitting thick white fumes of tellurous oxide. Tellurium is insoluble in hydrochloric acid,

but dissolves readily in nitric acid to tellurous oxide (TeO_2). Tellurium in powder dissolves in cold concentrated sulphuric acid to a purple-colored fluid, from which it separates again upon addition of water. TELLUROUS OXIDE is white; at a gentle red heat it fuses to a yellow fluid; it is volatilized by strong ignition in the air, forming no crystalline sublimate. It dissolves readily in hydrochloric acid, sparingly in nitric acid, freely in solution of potassa, slowly in ammonia, barely in water. TELLUROUS HYDROXIDE (H_2TeO_3) or TELLUROUS ACID is white; it is perceptibly soluble in cold water, and dissolves in hydrochloric acid and in nitric acid, forming tellurous chloride ($TeCl_4$) and nitrate ($Te(NO_3)_4$). Addition of water to these salts throws down the hydroxide again, and from the nitric acid solution tellurous oxide separates after some time as a crystalline precipitate. *Alkalies* and *alkali carbonates* throw down from tellurium chloride solution white hydroxide which is soluble in an excess of the precipitant. *Hydrogen sulphide* produces in acid solutions a brown precipitate of TELLUROUS SULPHIDE (TeS_2, in color like stannous sulphide), which dissolves very freely in ammonium sulphide. *Sodium sulphite, stannous chloride*, and *zinc* precipitate black metallic tellurium. By fusing tellurium or tellurites with alkali nitrates and carbonates ALKALI TELLURITES (*e.g.*, Na_2TeO_3) are formed. The fused mass is soluble in water. The solution remains clear upon acidifying with hydrochloric acid in the cold; but upon boiling chlorine is disengaged, and tellurous chloride formed, and the solution is therefore now precipitated by water if the excess of acid is not too great. If tellurium, its sulphide, or an oxygen compound of the metal is fused with *potassium cyanide* in a stream of hydrogen, a tellurium potassium cyanide is formed. The fused mass dissolves in water, but a current of air throws down from the solution the whole of the tellurium (difference and means of separating tellurium from selenium). When tested in the dry way by BUNSEN'S method (p. 30) the compounds of tellurium give a grayish-blue color in the upper reducing flame, while at the same time the upper oxidizing flame appears green. The volatilization is unaccompanied by any odor. The *incrustation produced by reduction* is black, with a blackish-brown edge, and gives a crimson solution when heated with concentrated sulphuric acid. The *incrustation of oxide* is white, scarcely visible; stannous chloride colors it black, metallic tellurium being separated. When heated with *sodium carbonate* in the *stick of charcoal*, compounds of tellurium yield sodium telluride, which when placed on clean silver and moistened produces a black stain, and when treated with hydrochloric acid (in the presence of enough tellurium) gives an odor of telluretted hydrogen with separation of tellurium.

e. SELENIUM, Se. 79.4.

SELENIUM occurs in nature in the form of selenides of metals. It is found occasionally in the dust of roasting-furnaces, and also in the Nordhausen oil of vitriol. It resembles sulphur in some respects, tellurium in others. Fused selenium is grayish-black; it volatilizes at a high temperature, and may be sublimed. Heated in the air it burns to selenious oxide (SeO_2), exhaling a characteristic smell of decaying horse-radish. Concentrated sulphuric acid dissolves selenium without oxidizing it; upon diluting the solution the selenium falls down in red flakes. Nitric acid and aqua regia dissolve selenium to SELENIOUS ACID ($SeO(OH)_2$). When the solution of the latter is evaporated

it loses water and is converted into selenious oxide, which at 200° volatilizes as a yellow gas. Sublimed selenious oxide appears in form of white four-sided needles, selenious acid in the form of crystals resembling those of potassium nitrate. Selenious oxide dissolves in water to selenious acid, making a strongly acid fluid. Of the normal salts only those with the alkali metals are soluble in water; the solutions have alkaline reactions. All selenites dissolve readily in nitric acid, with the exception of the selenites of lead and silver, which dissolve with difficulty. *Hydrogen sulphide* produces in solutions of selenious acid or of selenites (in presence of free hydrochloric acid) a yellow precipitate of SELENIUM SULPHIDE (?), which, upon heating, turns reddish-yellow, soluble in ammonium sulphide. *Barium chloride* produces (after neutralization of the free acid, should any be present), a white precipitate of BARIUM SELENITE, which is soluble in hydrochloric acid and in nitric acid. *Stannous chloride* or *sulphurous acid*, with addition of hydrochloric acid, produces a red precipitate of SELENIUM, which turns gray at a high temperature. *Metallic copper*, when placed in a warm solution of selenious acid containing hydrochloric acid, becomes immediately coated black; if the fluid remains long in contact with the copper, it turns light red from separation of selenium (REINSCH). By heating selenium or its compounds with alkali carbonates and nitrates, alkali SELENATES are formed. The fused mass dissolves in water; the solution remains clear upon acidifying with hydrochloric acid; when concentrated by boiling, it evolves chlorine, whilst the selenic acid ($Se O_2 (O H)_2$) is reduced to selenious acid. By fusing selenium or its compounds with *potassium cyanide* in a stream of hydrogen gas, a selenium potassium cyanide is obtained, from which the selenium is not eliminated by the action of the air (as is the case with tellurium); it separates, however, upon long-continued boiling, after addition of hydrochloric acid. When tested according to p. 30, compounds of selenium give a blue *color to the flame*, and by *volatilization* and combustion of the vapor the above-mentioned odor is emitted. The *incrustation produced by reduction* is brick-red to cherry-red, and gives a dirty green solution with concentrated sulphuric acid. The *incrustation of oxide* is white, and when moistened with stannous chloride becomes red from separated selenium. In the *charcoal stick* with *sodium carbonate* sodium selenide is formed, which when placed on silver and moistened produces a black stain, and when treated with acids yields selenetted hydrogen.

B.—DEPORTMENT OF THE ACIDS AND THEIR RADICALS.*

§ 136.

The reagents which serve for the detection of the acids are divided, like those used for the detection of the metals, into GENERAL REAGENTS, *i.e.*, such as indicate the GROUP to which the acid under examination belongs; and SPECIAL REAGENTS, *i.e.*, such as serve to effect the identification of the INDIVIDUAL ACIDS. These acid groups can scarcely be defined with the same degree of precision as those into which the bases are divided.

* Compare pp. 49, 50.

The two principal groups are those of INORGANIC and ORGANIC ACIDS. We base this division upon those characteristics by which the ends of analysis are most easily attained. We call *organic* those acids of which the salts—(particularly those of an alkali or an alkali-earth metal)—are decomposed upon ignition, with separation of carbon. A most simple preliminary experiment thus determines the class to which an acid belongs. The salts of organic acids with alkali or alkali-earth metals are converted into carbonates when heated gently to redness.

Before proceeding to the special study of the several acids, I give here a general view of the whole of them classified in groups.

I. INORGANIC ACIDS.

FIRST GROUP:

Division 1. *Chromic acid* (sulphurous and thiosulphuric acids, iodic acid). page 224.

Division 2. *Sulphuric acid* (hydrofluosilicic acid). page 228.

Division 3. *Phosphoric acid, boric acid, oxalic acid, hydrofluoric acid* (phosphorous acid). page 231.

Division 4. *Carbonic acid, silicic acid.* page 246.

SECOND GROUP:

Chlorine and *hydrochloric acid; bromine* and *hydrobromic acid; iodine* and *hydriodic acid; cyanogen* and *hydrocyanic acid,* together with *hydroferro-* and *hydroferricyanic acids; sulphur* and *hydrosulphuric acid* (*hydrogen sulphide*) (nitrous acid, hypochlorous acid, chlorous acid, hypophosphorous acid). page 251.

THIRD GROUP:

Nitric acid, chloric acid (perchloric acid). page 270.

II. ORGANIC ACIDS.

FIRST GROUP:

Oxalic acid, tartaric acid, citric acid, malic acid (racemic acid). page 275.

SECOND GROUP: page 284.

Succinic acid, benzoic acid.

THIRD GROUP:

Acetic acid, formic acid (lactic acid, propionic acid, butyric acid). page 286.

The acids printed in italics are more frequently met with in the examination of minerals, waters, ashes of plants, industrial products, medicines, etc.; the others are more rarely met with.

I. Inorganic Acids.

§ 137.

First Group.

Acids which are precipitated from Neutral Solutions by Barium Chloride.

This group is again subdivided into four divisions, viz.:

1. Acids which are decomposed in acid solution by hydrogen sulphide, and to which attention has therefore been directed already in the testing for bases, viz., CHROMIC ACID (sulphurous acid and thiosulphuric acid, the latter because it is decomposed and detected by the mere addition of hydrochloric acid to the solution of one of its salts; and also iodic acid).*
2. Acids which are not decomposed in acid solution by hydrosulphuric acid, and the barium compounds of which are insoluble in hydrochloric acid: SULPHURIC ACID (hydrofluosilicic acid).
3. Acids which are not decomposed in acid solution by hydrosulphuric acid, and the barium compounds of which dissolve in hydrochloric acid, apparently without decomposition, inasmuch as the acids cannot be completely separated from the hydrochloric acid solution by heating or evaporation; PHOSPHORIC ACID, BORIC ACID, OXALIC ACID, HYDROFLUORIC ACID (phosphorous acid). (Oxalic acid belongs more properly to the organic group. We consider it,

* To this first division of the first group of inorganic acids belong properly also all the oxygen compounds of a distinctly pronounced acid character, which have been discussed already with the Sixth Group of the metals (acids of arsenic, antimony, selenium, etc.). But as the reaction of these compounds with hydrosulphuric acid tends to lead to confounding them rather with other metals than with other acids, it appeared the safer course to class these compounds with the metallic radicals.

however, here with the acids of the inorganic class, as the property of its salts to be decomposed upon ignition without actual carbonization may lead to its being overlooked as an organic acid).

4. Acids which are not decomposed in acid solution by hydrosulphuric acid, and the barium salts of which are soluble in hydrochloric acid with separation of the acid: CARBONIC ACID, SILICIC ACID.

First Division of the First Group of the Inorganic Acids.

§ 138.

CHROMIC ACID, $Cr O_2 (O H)_2$ * (Cr. 52.5.)

1. CHROMIUM TRIOXIDE OR CHROMIC ANHYDRIDE appears as a scarlet crystalline mass, or in the form of distinct acicular crystals. Upon ignition it is resolved into chromic oxide, $Cr_2 O_3$, and oxygen. In deliquesces rapidly upon exposure to the air. It dissolves in water, imparting to the fluid a deep reddish-yellow tint, which remains visible in very dilute solutions.

The CHROMATES are all red or yellow, and for the most part insoluble in water. Part of them are decomposed upon ignition. Those with alkali bases are soluble in water; the solutions of the normal alkali chromates, *e.g.*, $K_2 Cr O_4$, † are yellow, those of the alkali dichromates (anhydrochromates or "bichromates"), *e.g.*, $K_2 Cr_2 O_7$ ‡ are reddish-yellow. These tints are visible in highly dilute solutions. The yellow color of the solution of a normal salt changes to reddish yellow on the addition of an acid.

3. *Hydrosulphuric acid* acting upon the acidified solution produces first a brownish coloration of the fluid, then a green coloration, arising from the formation of a chromic salt; this change of color is attended with separation of sulphur, which imparts a milky appearance to the fluid [$K_2 Cr_2 O_7 + 4 (H_2 S O_4) + 3 H_2 S = K_2 S O_4 + Cr_2 (S O_4)_3 + 3 S + 7 H_2 O$]. Heat promotes this reaction, part of the sulphur being in that case converted into sulphuric acid.

* The radical, $Cr O_2$, so analogous to $S O_2$, appears incapable of uniting with hydroxyl, since not only is chromic acid unknown as a distinct substance, but no chromates containing basic hydrogen exist.

† $Cr O_2 < \begin{matrix} O \\ O \end{matrix} \begin{matrix} K \\ K \end{matrix}$.

‡ $O < \begin{matrix} Cr\ O_2 - O \\ Cr\ O_2 - O \end{matrix} \begin{matrix} K \\ K \end{matrix} = K_2 Cr O_4 . Cr O_3$.

4. *Ammonium sulphide*, when added in excess to a solution of an alkali dichromate, immediately produces a bluish gray-green precipitate of CHROMIC HYDROXIDE; on boiling, the whole of the chromium separates as green chromic hydroxide. In a solution of normal potassium chromate at first a dark brownish coloration alone is produced, but the bluish gray-green precipitate above mentioned soon separates.

5. Chromic acid may also be reduced to chromic oxide by means of many other substances, and more particularly by *sulphurous acid*, by heating with concentrated *hydrochloric acid*, or with the dilute acid and alcohol (in which case ethyl chloride and aldehyde are evolved), by *metallic zinc*, by heating with *tartaric acid*, *oxalic acid*, etc. All these reactions are clearly characterized by the change of the red or yellow color of the solution to the green or violet tint of the chromic salt.

6. *Barium chloride* produces in aqueous solutions of chromates a yellowish-white precipitate of BARIUM CHROMATE, $Ba\ Cr\ O_4$, soluble in dilute hydrochloric and nitric acids.

7. *Silver nitrate* produces in aqueous solutions of chromates a dark purple-red precipitate of SILVER CHROMATE, $Ag_2\ Cr\ O_4$, soluble in nitric acid and in ammonia; in slightly acid solutions it produces a precipitate of SILVER DICHROMATE, $Ag_2\ Cr_2\ O_7$.

8. *Lead acetate* produces in an aqueous or acetic acid solution of a chromate a yellow precipitate of LEAD CHROMATE, $Pb\ Cr\ O_4$,* soluble in potassa, sparingly soluble in dilute nitric acid, insoluble in acetic acid. Upon heating with alkalies the yellow normal salt is converted into red diplumbic chromate, $Pb_2\ Cr\ O_5$.†

9. If a very dilute acid solution of *hydrogen dioxide* ‡ (about 6 or 8 c.c.) is covered with a layer of ether (about half a centimetre thick), and a fluid containing chromic acid is added, the solution of hydrogen dioxide acquires a fine blue color. By inverting the test tube, closed with the thumb, repeatedly, without much shaking, the solution becomes colorless, whilst the ether acquires a blue color. The latter reaction is particularly characteristic. One part of potassium chromate in 40,000 parts of water suffices to produce it distinctly (STORER); presence of vanadic acid materially impairs the delicacy of the test (WERTHER).§ The cause of this blue coloration is not certainly known. After some time the ether is decolorized.

10. If insoluble chromates are fused with *sodium carbonate*

* $Cr\ O_2 < \begin{matrix} O \\ O \end{matrix} > Pb$. † $Pb\ Cr\ O_4 . Pb\ O = O < \begin{matrix} Pb-O \\ Pb-O \end{matrix} > Cr\ O_2$.

‡ Solution of hydrogen dioxide may be easily prepared by triturating a fragment of barium dioxide (about the size of a pea) with some water, and adding it with stirring to a mixture of about 30 c.c. hydrochloric acid, and 120 c.c. water. The solution keeps a long time without suffering decomposition. In default of barium dioxide impure sodium dioxide may be used instead, which is obtained by heating a fragment of sodium in a porcelain capsule until it takes fire, and letting it burn.

§ Journ. f. prakt. Chem. 83, 195.

and *nitrate*, and the fused mass is treated with water, the fluid obtained appears yellow from the alkali chromate which it holds in solution; upon the addition of an acid the yellow color changes to reddish-yellow. The bases are left either as oxides or carbonates, unless they are soluble in the sodium hydroxide formed from the nitrate.

11. The alkali chromates show the same reactions with *sodium metaphosphate* and with *borax* in the blowpipe flame, as chromic oxide and chromium salts.

12. Very minute quantities of chromic acid may be detected by one of the following methods: *a*. Mix with the fluid, slightly acidified with sulphuric acid, a little tincture of guaiacum (1 part of the resin to 100 parts of alcohol of 60 per cent.) when an intense blue coloration of the fluid will at once make its appearance, speedily vanishing again, however, where mere traces of chromic acid are present (H. SCHIFF); *b*. mix the solution of the alkali chromate, which must be as neutral as possible, with some dilute decoction of logwood, when a very intense black coloration will be produced; in the presence of exceedingly small quantities of chromic acid the color is violet-red (R. WILDENSTEIN).

Chromic acid being reduced by hydrosulphuric acid to chromic oxide, this acid is in the course of analysis always found in the examination for bases. The intense color of the solutions containing chromic acid, the excellent reaction with hydrogen dioxide, and the characteristic precipitates produced by solutions of lead salts and silver salts, afford moreover ready means for its detection. For the discovery of traces of chromium present in many minerals, for instance in serpentine, the reactions in 12 may be used after the mineral has been fused with sodium carbonate and nitrate.

Rarer Acids of the First Division.

§ 139.

a. SULPHUROUS ACID, H_2SO_3.

SULPHUR DIOXIDE OR SULPHUROUS ANHYDRIDE, SO_2, is a colorless, uninflammable gas, which has the stifling odor of burning sulphur. It dissolves copiously in water. The solution, in which we may assume the existence of SULPHUROUS ACID, H_2SO_3, has the odor of the gas, reddens litmus paper, and bleaches Brazil-wood paper. Sulphurous acid absorbs oxygen from the air, and is thereby converted into sulphuric acid. The salts are colorless. Of the normal sulphites, those with alkali base only are readily soluble in water; many of the sulphites insoluble or sparingly soluble in water dissolve in an aqueous solution of sulphurous acid, but fall down again on boiling. All the sulphites

evolve sulphur dioxide when treated with *sulphuric acid*. *Chlorine water* dissolves most sulphites to sulphates. *Barium chloride* precipitates normal sulphites, but not free sulphurous acid. The precipitate dissolves in hydrochloric acid. *Hydrosulphuric acid* decomposes the free sulphurous acid, water and pentathionic acid being formed with separation of sulphur. If to a solution of sulphurous acid, mixed with an equal volume of hydrochloric acid, a piece of clean *copper* wire is added, and the mixture is boiled, the copper appears black, as if covered with soot, if much sulphurous acid is present; but only dull if little is present (H. REINSCH). If a trace of sulphurous acid or of a sulphite is introduced into a flask in which hydrogen is being evolved from *zinc* or *aluminium* and *hydrochloric acid*, hydrosulphuric acid is immediately evolved along with the hydrogen, and the gas now produces a black coloration or a black precipitate in a solution of lead acetate to which has been added a sufficient quantity of soda to redissolve the precipitate which forms at first. Sulphurous acid is a powerful reducing agent: it reduces chromic acid, permanganic acid, mercuric chloride (to mercurous chloride), decolorizes iodized starch, produces a blue precipitate in a mixture of potassium ferricyanide and ferric chloride, etc. With a hydrochloric acid solution of *stannous chloride* a yellow precipitate of STANNIC SULPHIDE is formed after some time. If an aqueous solution of an alkali sulphite is mixed with acetic acid just to give it an incipient acid reaction, and is then added to a relatively large amount of solution of *zinc sulphate* mixed with a very small quantity of *sodium nitroprusside*, the fluid acquires a red color if the quantity of sulphite present is not too inconsiderable, but when the quantity of the sulphite is very minute the coloration makes its appearance only after addition of some solution of potassium ferrocyanide. If the quantities are not altogether too minute, a purple-red precipitate will form upon the addition of the potassium ferrocyanide (BÖDEKER). Thiosulphates of the alkalies do not show this reaction.

b. THIOSULPHURIC (HYPOSULPHUROUS) ACID, $H_2S_2O_3$.

This acid does not exist in the free state. Most of its salts are soluble in water. The solutions of most thiosulphates may be boiled without suffering decomposition; calcium thiosulphate is resolved upon boiling into calcium sulphite and sulphur. If *hydrochloric acid* or *sulphuric acid* is added to the solution of a thiosulphate, the fluid remains at first clear and inodorous, but after a short time—the shorter the more concentrated the solution—it becomes more and more turbid, owing to the separation of sulphur, and exhales the odor of sulphur dioxide. Application of heat promotes this decomposition. *Silver nitrate* produces a white precipitate of SILVER THIOSULPHATE, which is soluble in an excess of the thiosulphate; after a little while (upon heating almost immediately) this precipitate turns black, being decomposed into silver sulphide and sulphuric acid. Sodium thiosulphate dissolves silver chloride; upon the addition of an acid the solution remains clear at first, but after some time, and immediately upon boiling, silver sulphide separates. *Barium chloride* produces a white precipitate, which is soluble in much water more especially hot water, and is decomposed by hydrochloric acid. *Ferric chloride* colors the solutions of alkali thiosulphates reddish-violet (here they differ from alkali sulphites); on standing the liquid loses its color, especially when heated, ferrous chloride being formed. Acidified solution of *chromic acid* is immediately reduced by thiosulphates, *iodized starch* is at once decolorized.

With *zinc* or *aluminium* and *hydrochloric acid* the thiosulphates behave like the sulphites.

Where it is required to find sulphites and thiosulphates of the alkali metals in presence of alkali sulphides, as is often the case, solution of zinc sulphate is first added to the fluid until the sulphide is decomposed; the zinc sulphide is then filtered off, and one part of the filtrate is tested for thiosulphuric acid by addition of hydrochloric acid, another portion for sulphurous acid with sodium nitroprusside, etc.

c. Iodic Acid, $H I O_3$.

Iodic acid crystallizes in white, six-sided tables or rhombic crystals; at a moderate heat it is resolved into iodine vapor and oxygen; it is readily soluble in water. The salts are decomposed upon ignition, being resolved either into oxygen and a metallic iodide, or into iodine, oxygen, and metallic oxide: the iodates with an alkali base alone dissolve readily in water. *Barium chloride* throws down from solution of iodates of the alkali metals a white precipitate of barium iodate, which is soluble in nitric acid; *silver nitrate* a white granular crystalline precipitate of silver iodate, which dissolves readily in ammonia, but only sparingly in nitric acid. *Hydrosulphuric acid* throws down from solutions of iodic acid iodine, which then dissolves in hydriodic acid; the precipitation is attended with separation of sulphur. If an excess of hydrosulphuric acid is added, the fluid loses its color, and a further separation of sulphur takes place, the iodine being converted into hydriodic acid. Iodic acid combined with bases is also decomposed by hydrosulphuric acid. *Sulphurous acid* throws down iodine, which upon addition of an excess of the acid is converted into hydriodic acid. Addition of *pure* $H Cl$ or $H_2 S O_4$, to an iodate in presence of $K I$ causes separation of iodine which tinges the liquid yellow and may be further identified with starch paste.

Second Division of the First Group of the Inorganic Acids.

Sulphuric Acid, $H_2 S O_4$, (S. 32.)

§ 140.

1. Sulphur trioxide or sulphuric anhydride, $S O_3$, is a white feathery crystalline mass which emits strong fumes upon exposure to the air; sulphuric acid, $H_2 S O_4$, forms an oily liquid, colorless and transparent like water. Both the anhydride and the acid char organic substances, and combine with water in all proportions, the process of combination being attended with considerable elevation of temperature, and in the case of the anhydride with a hissing noise.

2. The normal sulphates are readily soluble in water, with the exception of the sulphates of barium, strontium, calcium, and lead. The basic sulphates of the heavy metals which are insoluble in water dissolve in hydrochloric acid or in nitric acid. Most of the sulphates are colorless or white. The sulphates of the alkali metals are not decomposed by

ignition. The other sulphates are acted upon differently by a red heat, some of them being readily decomposed, others with difficulty, and some resisting decomposition altogether.

3. *Barium chloride* produces, even in exceedingly dilute solutions of sulphuric acid and of the sulphates, a finely pulverulent, heavy, white precipitate of BARIUM SULPHATE ($Ba S O_4$), insoluble in dilute hydrochloric and nitric acids. From very dilute solutions the precipitate separates only after standing for some time. Concentrated acids and concentrated solutions of many salts impair the delicacy of the reaction.

4. *Lead acetate* produces a heavy white precipitate of LEAD SULPHATE ($Pb S O_4$) which is sparingly soluble in dilute nitric acid, but dissolves completely in hot concentrated hydrochloric acid.

5. The sulphates of the alkali-earth metals which are insoluble in water and acids are converted into CARBONATES by fusion with *alkali carbonates*. But lead sulphate yields LEAD OXIDE when treated in this manner. In both cases an alkali sulphate is formed. The sulphates of the alkali-earth metals and of lead are also resolved into insoluble carbonates and soluble alkali sulphate by digestion or boiling with concentrated solutions of carbonates of the alkali metals (comp. §§ 95, 96, 97).

6. Upon fusing sulphates with *sodium carbonate* on *charcoal* in the inner flame of the blowpipe, or heating them in the stick of charcoal (p. 31) in the lower reducing flame, the sulphuric acid is reduced, and sodium sulphide formed, which may be readily recognized by the odor of hydrosulphuric acid emitted upon moistening the sample and the part of the charcoal into which the fused mass has penetrated, and adding some acid. If the fused mass is transferred to a clean silver plate, or a polished silver coin, and then moistened with water and some acid, a black stain of silver sulphide is immediately formed. (Compounds of tellurium and selenium give the same reaction.)

Remarks.—The characteristic and exceedingly delicate reaction of SULPHURIC ACID with barium salts renders the detection of this acid an easier task than that of almost any

other. It is simply necessary to take care not to confound with barium sulphate precipitates of barium chloride, and particularly of barium nitrate, which are formed upon mixing aqueous solutions of these salts with fluids containing a large proportion of free hydrochloric acid or free nitric acid. It is very easy to distinguish these precipitates from barium sulphate, since they redissolve immediately upon diluting the acid fluid with water. It is a rule that should never be departed from, in testing for sulphuric acid with barium chloride, to dilute the fluid largely; a little hydrochloric acid should also be added, which counteracts the adverse influence of many salts, as, for instance, citrates of the alkali metals. Where very minute quantities of sulphuric acid are to be detected the fluid should be allowed to stand several hours at a gentle heat; the trace of barium sulphate formed will in that case be found deposited at the bottom of the vessel. When the least uncertainty exists about the nature of the precipitate produced by barium chloride in presence of hydrochloric acid, the reaction in 6, will at once set all doubt at rest. In looking for very small quantities of sulphuric acid in the presence of much hydrochloric or nitric acid, the greater part of the latter should first be evaporated off or neutralized. To detect *free sulphuric acid* in presence of a sulphate the fluid is mixed with a very little cane-sugar, and evaporated to dryness in a porcelain dish at 100°. If free sulphuric acid was present a black residue remains, or in the case of most minute quantities, a blackish-green residue. Other free acids do not decompose cane-sugar in this way.

§ 141.

Hydrofluosilicic Acid, $2\,H\,F\,.\,Si\,F_4$.

Hydrofluosilicic acid is a very acid fluid; upon evaporation on platinum it volatilizes completely as silicon fluoride and hydrofluoric acid. When evaporated in glass it etches the latter. With bases it forms water and silico-fluorides of the metals, which are most of them soluble in water, redden litmus paper, and are resolved upon ignition into metallic fluorides and silicon fluoride. *Barium chloride* forms a crystalline precipitate with hydrofluosilicic acid (§ 95, 6). *Strontium chloride* and *lead acetate* form no precipitate with this acid. *Potassium salts* precipitate transparent gelatinous POTASSIUM SILICO-FLUORIDE; *ammonia* in excess precipitates SILICIC ACID, with formation of ammonium fluoride. By heating metallic silico-fluorides with concentrated

sulphuric acid dense fumes are emitted in the air, arising from the evolution of hydrofluoric and silicofluoric gas. If the experiment is conducted in a platinum vessel covered with glass the fumes ETCH the glass (§ 146, 5); the residue contains the sulphates formed.

Third Division of the First Group of the Inorganic Acids.

§ 142.

a. PHOSPHORUS, P. 31, AND ORTHOPHOSPHORIC ACID OR TRIHYDROGEN PHOSPHATE, H_3PO_4 or $PO(OH)_3$.

1. COMMON PHOSPHORUS is a colorless, transparent, solid body, of 1.84 specific gravity; it has a waxy appearance. Taken internally it acts as a virulent poison. It fuses at 44.3°, and boils at 290°. By the influence of light, phosphorus kept under water turns first yellow, then red, and is finally covered with a white crust. If phosphorus is exposed to the air at the common temperature, it exhales a highly characteristic and most disagreeable odor, copious fumes being evolved which are luminous in the dark. These fumes are formed by oxidation of the vapor of phosphorus, and consist of phosphoric and phosphorous acids. When the air is moist, ozone, hydrogen dioxide, and ammonium nitrite are produced at the same time. Phosphorus very readily takes fire, burning with a luminous flame to phosphoric oxide, which appears in the form of white fumes. By the protracted influence of light, or by heating to 250°, phosphorus is converted into RED (so-called amorphous) PHOSPHORUS. Red phosphorus does not alter in the air, it is not luminous, its inflammability is much decreased, and it has a specific gravity of 2.1. Nitric acid and nitrohydrochloric acid dissolve phosphorus pretty readily upon heating. The solutions contain at first, besides phosphoric acid, also phosphorous acid. Hydrochloric acid does not dissolve phosphorus. If phosphorus is boiled with solution of soda or potassa, or with milk of lime, hypophosphites and phosphates are formed, whilst spontaneously inflammable phosphoretted hydrogen gas escapes. If a substance containing unoxidized phosphorus is placed at the bottom of a flask, and a slip of paper moistened with solution of silver nitrate is by means of a cork loosely inserted into the mouth suspended inside the flask, and a gentle heat applied (from 30° to 40°), the paper slip will turn black in consequence of the reducing action of the phosphorus fumes, even though only a most minute quantity of the phosphorus should be present. If after the termination of the reaction the blackened part of the paper is boiled with water, the undecomposed portion of the silver salt precipitated with hydrochloric acid, the fluid filtered, and the filtrate evaporated as far as practicable on the water-bath, the presence of phosphoric acid in the residue may be shown by means of the reactions described below (J. SCHERER). It must be borne in mind that the silver salt is blackened also by hydrosulphuric acid, formic acid, volatile products of putrefaction, etc., and also that the detection of phosphoric acid in the slip of paper can be of value only where the latter and the filtering paper were perfectly free from phosphorus. As regards the deportment of phosphorus upon boiling with dilute sulphuric acid, and in a hydrogen evolution apparatus supplied with zinc and dilute sulphuric acid, see § 220.

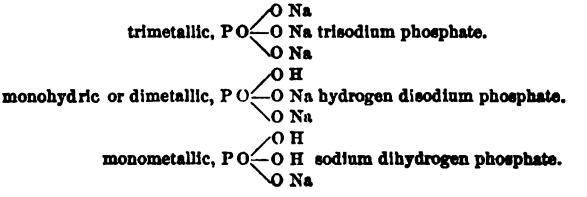
2. PHOSPHORIC OXIDE (PHOSPHORIC ANHYDRIDE), P_2O_5, is a white, snow-like mass, which rapidly deliquesces in the air. When treated with water it hisses like a red-hot iron, and is at first only partially dissolved, in time, however, the solution is complete. It forms with water and bases three series of compounds, viz., with three molecules of water or of base, orthophosphoric acid or common phosphates, *e.g.*, $P_2O_5 + 3H_2O = 2[PO(OH)_3]$; with two molecules of water or of base, pyrophosphoric acid or pyrophosphates; with one molecule of water or of base, metaphosphoric acid or metaphosphates. As the meta- and pyrophosphoric acids are comparatively rare, they will be treated in a supplemental paragraph.

3. The ORTHOPHOSPHORIC ACID,* $PO(OH)_3$, forms colorless and pellucid crystals, which deliquesce rapidly in the air to a syrupy non-caustic liquid. The action of heat changes it into meta- or pyrophosphoric acid, according as either one or two molecules of water are expelled. Heated in an open platinum dish orthophosphoric acid, if pure, volatilizes completely, though with difficulty, in white fumes. Orthophosphoric acid forms three series of salts, monometallic, dimetallic, or monohydric, and trimetallic, according to the extent to which its hydroxyl is replaced by basic radicals.†

4. The action of heat fails to decompose the ORTHOPHOSPHATES with fixed bases, but converts them into pyrophosphates if they contain one hydroxyl or one ammonium, and into metaphosphates if they contain two hydroxyls or other volatile radicals. Of the normal orthophosphates those with alkali bases alone are soluble in water. The solutions manifest alkaline reactions. If pyro- or metaphosphates are fused with excess of sodium carbonate, the fused mass contains only orthophosphates.

* The names *phosphoric acid* and *phosphates*, when not qualified by prefixes, apply to the ortho compounds.

† The univalent basic radicals form three phosphates, *e.g.*,

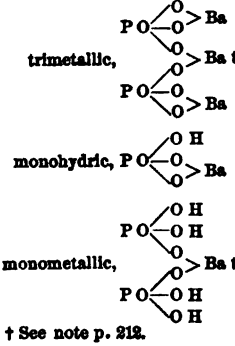

trimetallic, PO(ONa)(ONa)(ONa) trisodium phosphate.
monohydric or dimetallic, PO(OH)(ONa)(ONa) hydrogen disodium phosphate.
monometallic, PO(OH)(OH)(ONa) sodium dihydrogen phosphate.

5. *Barium chloride* does not precipitate aqueous solutions of orthophosphoric acid. In aqueous solutions of dimetallic phosphates of the alkali metals it produces a white precipitate of HYDROGEN BARIUM PHOSPHATE, $BaHPO_4$. In solutions of trimetallic (normal) phosphates it gives white TRIBARIUM PHOSPHATE, $Ba_3(PO_4)_2$.* Both precipitates are soluble in hydrochloric and nitric acids, but sparingly soluble in chloride of ammonium.

6. Solution *of calcium sulphate* produces in neutral or alkaline solutions of phosphates, but not in solutions of phosphoric acid, a white precipitate of HYDROGEN CALCIUM PHOSPHATE, $CaHPO_4$, or of TRICALCIUM PHOSPHATE, $Ca_3(PO_4)_2$, which dissolves readily in acids, even in acetic acid, and is soluble also in ammonium chloride.

7. *Magnesium sulphate* produces in concentrated solutions of dimetallic alkali phosphates, a white precipitate of HYDROGEN MAGNESIUM PHOSPHATE, $MgHPO_4 + aq$, which often separates only after some time; upon boiling, a precipitate of TRIMAGNESIUM PHOSPHATE, $Mg_3(PO_4)_2 + 2\frac{1}{2}\,aq$, is thrown down immediately. The latter precipitate forms also upon addition of magnesium sulphate to the solution of a trimetallic alkali phosphate. But if a mixture † of magnesium sulphate and ammonia with sufficient ammonium chloride to hold in solution or to redissolve magnesium hydroxide is added to a solution of phosphoric acid or of an alkali phosphate, a white crystalline and quickly subsiding precipitate of AMMONIUM MAGNESIUM PHOSPHATE, $NH_4MgPO_4 + 6\,aq$, is formed, even in highly dilute solutions. This precipitate is insoluble in ammonia, and most sparingly soluble in ammonium chloride, but dissolves readily in acids, even in acetic acid. It makes

* Barium and other bivalent basic radicals, with or without hydrogen, form three phosphates, viz.:


trimetallic,
Ba tribarium phosphate (basic phosphate of baryta).
monohydric,
hydrogen barium phosphate (neutral phosphate of baryta).
monometallic,
Ba tetrahydrogen barium phosphate (acid phosphate of baryta).

† See note p. 212.

its appearance often only after the lapse of some time; stirring promotes its separation (§ 98, 8). The reaction can be considered decisive only if no arsenic acid is present (§ 133, 9).

8. *Silver nitrate* throws down from solutions of di- and trimetallic alkali phosphates a light-yellow precipitate of SILVER PHOSPHATE, Ag_3PO_4, which is readily soluble in nitric acid and in ammonia. If the solution contained a trimetallic phosphate the fluid in which the precipitate is suspended manifests a neutral reaction, whilst the reaction is acid if the solution contained a dimetallic phosphate. The acid reaction in the latter case arises from the circumstance that the nitric radical receives, for the 3 atoms of silver which it yields to the phosphoric acid, only 2 atoms of alkali metal and 1 atom of hydrogen, $K_2HPO_4 + 3(AgNO_3) = Ag_3PO_4 + 2(KNO_3) + HNO_3$.

9. If to a solution containing phosphoric acid and the *least possible excess* of hydrochloric or nitric acid a tolerably large amount of *sodium acetate* is added, and then a drop of *ferric chloride*, a yellowish-white, flocculent, gelatinous precipitate of FERRIC PHOSPHATE ($Fe_2(PO_4)_2 + 2$ aq) is formed. An excess of ferric chloride must be avoided, as ferric acetate (of red color) would thereby be formed, in which the precipitate is not insoluble. This reaction is of importance, as it enables us to detect phosphoric acid in phosphates of the alkali-earth metals; but it can be held to be decisive only if no arsenic acid is present, as this shows the same reaction. To effect the complete separation of phosphoric acid from the alkali-earth metals a sufficient quantity of ferric chloride is added to impart a reddish color to the solution, which is then boiled (whereby the whole of the iron is thrown down, partly as phosphate, partly as basic acetate), and filtered hot. The filtrate contains the alkali-earth metals as chlorides. If you wish to detect, by means of this reaction, phosphoric acid in presence of a large proportion of ferric salts, boil the hydrochloric acid solution with sodium sulphite until the ferric chloride is reduced to ferrous chloride, as indicated by decoloration; add sodium carbonate until the fluid is nearly neutral, then sodium acetate, and finally one drop of ferric chloride. The reason for this proceeding is, that ferrous acetate does not dissolve ferric phosphate.

10. When a neutral or acid solution containing phosphoric acid is mixed with solution of *ammonium molybdate in nitric acid* (§ 55), there is usually formed, immediately or in a short time, a pulverulent pale yellow precipitate of AMMONIUM PHOSPHO-MOLYBDATE,* which gathers upon the sides and bottom of

* [According to Gibbs there appear to be at least three distinct salts quite similar in color and insolubility, having the formulæ:

$48\,MoO_3 . 2\,P_2O_5 . 5\,(NH_4)_2O . 17\,H_2O$, containing 3.66 per cent. P_2O_5,
$22\,MoO_3 . P_2O_5 . 3\,(NH_4)_2O . 9\,H_2O$, " 3.91 " "
and $60\,MoO_3 . 3\,P_2O_5 . 8\,(NH_4)_2O . 12\,H_2O$, " 4.39 " "].

the test tube. This precipitate is soluble in phosphoric and hydrochloric acid, and in solutions of phosphates and chlorides, and may fail to appear when these are present in large proportion. It is totally insoluble in the "molybdic solution" (§ 55). *Accordingly if the latter be added in considerable excess* very small quantities of phosphoric acid are completely precipitated. It is best therefore at first to add the solution to be tested slowly, drop by drop, to several centimeter-cubes of the molybdic solution. Only when the phosphoric acid is present in exceedingly minute quantity, *e.g.*, 0.00002 grm., is it requisite to wait some hours and to apply *a gentle heat, not to exceed* 40° *C.*, before the precipitate appears. When other coloring matters are not present, the liquid above the precipitate is colorless. *A yellow coloration of the liquid is not to be regarded as proof of the presence of phosphoric acid.*

By operating in the manner above described, there is little danger of mistaking any other substance for phosphoric acid. Arsenic acid gives *in the cold*, no precipitate with the molybdic solution, although indeed, a yellow precipitate is formed on heating and especially on boiling. The liquid above the arsenical precipitate has a yellow color. Silicic acid does not react at all with molybdic solution in the cold. On heating it causes a strong yellow coloration, and when abundant may give a yellow precipitate. It is therefore best to separate arsenic and silicic acids when the liquid above the precipitate has a yellow color, and to repeat the test in their absence.

The PHOSPHO-MOLYBDATE OF AMMONIUM contains only a small amount (from 1.6 to 1.9 *per cent.*) of PHOSPHORUS. The precipitate is easily recognized even in dark-colored liquids, by giving it time to settle. If it be washed with the same molybdic solution employed in producing it and be then dissolved in ammonia, addition of "magnesia mixture" (see note p. 212), to the solution will throw down ammonium magnesium phosphate.

11. If a finely powdered substance containing phosphoric acid (or a metallic phosphide) is intimately mixed with 5 parts of a flux consisting of 3 parts of sodium carbonate, 1 part of sodium nitrate, and 1 part of silicic acid, the mixture fused in a platinum spoon or crucible, the fused mass boiled with water, the solution obtained decanted, ammonium carbonate added to it, the fluid boiled again, and the silicic acid which is thereby precipitated filtered off, the

filtrate now holds in solution alkali phosphate, and may accordingly be tested for phosphoric acid as directed in 7, 8, 9, or 10.

12. On igniting and pulverizing a substance containing phosphoric acid, placing it into a tube of the thickness of a straw and sealed at one end, adding a fragment of magnesium wire about two lines long (or a small piece of sodium), which should be covered by the sample, and then heating, a vivid incandescence will be observed and magnesium (or sodium) phosphide will be formed. When the black contents of the tube are crushed and moistened with water they exhale the characteristic odor of phosphoretted hydrogen. (WINKELBLECH, BUNSEN.)

13. *White of egg* is not precipitated by solution of orthophosphoric acid, nor by solutions of orthophosphates mixed with acetic acid.

§ 143.

a. Pyrophosphoric acid or *tetrahydrogen phosphate*, $H_4 P_2 O_7$. The solution of pyrophosphoric acid is converted by boiling into solution of orthophosphoric acid, $H_4 P_2 O_7 + H_2 O = 2 (H_3 P O_4)$. The solutions of the salts bear heating without suffering decomposition, but upon boiling with a strong acid the pyrophosphoric acid is converted into orthophosphoric acid. If the salts are fused with sodium carbonate in excess, orthophosphates are produced. Of the tetrametallic pyrophosphates only those with alkali base are soluble in water; the acid salts, *e. g.*, $Na_2 H_2 P_2 O_7$, are by ignition converted into metaphosphates, *e. g.*, $Na P O_3$. *Barium chloride* fails to precipitate the free acid; from solutions of the salts it precipitates white BARIUM PYROPHOSPHATE, $Ba_2 P_2 O_7$, soluble in hydrochloric acid. *Silver nitrate* throws down from a solution of the acid, especially upon addition of an alkali, a white earthy-looking precipitate of SILVER PYROPHOSPHATE, $Ag_4 P_2 O_7$, which is soluble in nitric acid and in ammonia. *Magnesium sulphate* precipitates MAGNESIUM PYROPHOSPHATE, $Mg_2 P_2 O_7$. The precipitate dissolves in an excess of the pyrophosphate, as well as in an excess of the magnesium sulphate. Ammonia fails to precipitate it from these solutions. Upon boiling the solution it separates again (means of detecting pyrophosphoric acid in presence of phosphoric acid). A concentrated solution of *luteo-cobaltic chloride* added to an alkali pyrophosphate produces an immediate precipitation of pale reddish-yellow spangles. (Here pyrophosphoric acid differs from phosphoric and metaphosphoric acids.—C. D. BRAUN.) *White of egg* is not precipitated by solution of the acid, nor by solutions of the salts mixed with acetic acid. *Ammonium molybdate*, with addition of nitric acid, fails to produce a precipitate.

b. Metaphosphoric acid. Five sorts of metaphosphates are known, and the acids also corresponding to most of these have been produced. The several reactions by which to distinguish between these I will not enter upon here, and confine myself to the simple observation that the metaphosphoric acids differ from the pyro- and orthophosphoric acid in this, that the solutions of the metaphosphoric acids precipitate *white of egg* at once, and the solutions of their salts after addition of acetic acid. Those acids and salts which are precipitated by *silver nitrate* produce with that reagent a white precipitate. A mixture of *magnesium sulphate*, ammonium chloride and ammonia fails to

precipitate the metaphosphoric acids and their salts, or produces precipitates soluble in ammonium chloride. All metaphosphates yield upon fusion with sodium carbonate, sodium orthophosphate.

§ 144.

b. Boric or Boracic Acid. $B(OH)_3$ (B. 11.)

1. Boric oxide, B_2O_3, is a colorless, fixed glass, fusible at a red heat. Orthoboric acid, $B(OH)_3$, appears as small, scaly crystals; on heating to 100° C., it is transformed into metaboric acid, BO(OH), a porous white mass. Orthoboric acid is soluble in water and in alcohol; upon evaporating the solutions a large proportion of boric acid volatilizes along with the aqueous and alcoholic vapors. The solutions redden litmus paper, and impart to turmeric paper a faint brown-red tint, which acquires intensity upon drying. The borates are not decomposed upon ignition; those with alkali bases alone are readily soluble in water. The solutions of borates of the alkali metals are colorless, and all of them, even those of the acid salts, manifest alkaline reaction.

2. *Barium chloride* produces in solutions of borates, if not too highly dilute, white precipitates of barium borate, which are soluble in much water as well as in acids and ammonium salts. The composition of these precipitates depends upon that of the borates in whose solutions they are formed, as well as upon the temperature and dilution of the liquid.

3. *Calcium chloride* deports itself toward solutions of borates the same as barium chloride.

4. *Silver nitrate* produces in concentrated solutions of borax a white precipitate which dissolves in a large amount of water. If the borax solution is first diluted with nearly enough water to dissolve the silver borate, the addition of silver nitrate produces a brown precipitate of silver oxide. All these precipitates dissolve in nitric acid and in ammonia.

5. If dilute *sulphuric acid* or *hydrochloric acid* is added to highly concentrated, hot prepared solutions of alkali borates, orthoboric acid separates upon cooling, in the form of shining crystalline scales.

6. If *alcohol* is poured over free boric acid or a borate—with addition, in the latter case, of *a sufficient quantity of concentrated sulphuric acid* to liberate the boric acid—and the alcohol

is kindled, the flame appears of a very distinct YELLOWISH-GREEN color, especially upon stirring the mixture; this tint is imparted to the flame by the boric acid which volatilizes with the alcohol. The delicacy of this reaction may be considerably heightened by heating the dish which contains the alcoholic mixture, kindling the alcohol, allowing it to burn for a short time, then extinguishing the flame, and afterwards rekindling it. At the first flickering of the flame its borders will now appear green, even though the quantity of the boric acid be so minute that it fails to produce a perceptible coloring of the flame when treated in the usual manner. As salts of copper also impart a green tint to the flame of alcohol, the copper which might be present must first be removed by means of hydrogen sulphide. Presence of metallic chlorides also may lead to mistakes, as the ethyl chloride formed in that case colors the borders of the flame bluish-green.

7. If a solution of boric acid, or of a borate of an alkali metal or of an alkali-earth metal, is mixed with hydrochloric acid to slight, but distinct, acid reaction, and a slip of *turmeric paper* is half dipped into it, and then dried on a watch glass at 100°, the dipped half shows a peculiar RED tint (H. ROSE).

This reaction is very delicate; care must be taken not to confound the characteristic red coloration with the blackish-brown color which turmeric paper acquires when moistened with rather concentrated hydrochloric acid and then dried; nor with the brownish-red coloration which ferric chloride, or a hydrochloric acid solution of ammonium molybdate or of zirconia gives to turmeric paper, more particularly upon drying. By moistening turmeric paper reddened by boric acid with a solution of an alkali or an alkali carbonate, the color is changed to bluish-black or greenish-black; but a little hydrochloric acid will at once restore the brownish-red color (A. VOGEL, H. LUDWIG).

8. If a substance containing boric acid is reduced to a fine powder, this with addition of a drop of water mixed with 3 parts of a flux composed of 4½ parts of potassium disulphate and one part of finely pulverized calcium fluoride, free from boric acid, and the paste exposed on the loop of a platinum wire in the outer mantle of the Bunsen gas flame, or at the apex of the inner flame of the blowpipe, boron fluoride escapes, which imparts to the flame—though only for an instant—a green tint. With readily decomposed compounds the reaction may be obtained by simply moistening the sample with hydrofluosilicic acid, and holding it in the flame.

9. Boric acid or borates, fused with sodium carbonate on the loop of a platinum wire, give, when placed in the flame of the *spectrum apparatus*, a spectrum of four well-marked lines of equal width, equidistant from each other. B_1 is brilliant yellowish-green (coinciding with Ba γ), B_2 is brilliant light-green (coinciding with Ba β), B_3 is pale bluish-green (nearly coinciding with the blue barium line), B_4 is blue, very pale, close to Sr δ (SIMMLER).

§ 145.

c. OXALIC ACID, $C_2H_2O_4 = C_2O_2(OH)_2 = \bar{O}$.*

1. OXALIC ACID is a white powder; the CRYSTALLIZED ACID, $C_2H_2O_4 + 2H_2O$, forms colorless rhombic prisms. Both dissolve readily in water and in alcohol. By heating rapidly in open vessels part of the acid undergoes decomposition whilst another portion volatilizes unaltered. The fumes of the volatilizing acid are very irritating and provoke coughing. If the acid is heated in a test-tube part of it sublimes unaltered.

2. The OXALATES undergo decomposition at a red heat yielding carbon monoxide and carbon dioxide. The oxalates of the alkali metals, and of barium, strontium and calcium are in this process converted into carbonates (if pure, and if the heat is gentle, almost without separation of charcoal). Magnesium oxalate is converted into magnesia even by a very gentle red heat. The other metallic oxalates leave either the pure metal or an oxide behind, according to the reducibility of the metallic oxide. The alkali metal oxalates and some others are soluble in water.

3. *Barium chloride* produces in neutral solutions of alkali oxalates a white precipitate of BARIUM OXALATE, BaC_2O_4, which dissolves very sparingly in water, more readily in water containing ammonium chloride, acetic acid, or oxalic acid, freely in nitric acid and in hydrochloric acid; ammonia precipitates it from the latter solutions unaltered.

4. *Silver nitrate* produces in solutions of oxalic acid and of alkali oxalates a white precipitate of SILVER OXALATE, $Ag_2C_2O_4$, which is readily soluble in concentrated hot nitric acid and

* Oxalic acid = $\begin{matrix}COOH\\|\\COOH\end{matrix}$; Sodium oxalate = $\begin{matrix}COONa\\|\\COONa\end{matrix}$;

Hydrogen sodium oxalate = $\begin{matrix}COOH\\|\\COONa\end{matrix}$; Calcium oxalate = $\begin{matrix}COO\\COO\end{matrix}>Ca$.

also in ammonia, but dissolves with difficulty in dilute nitric acid, and is most sparingly soluble in water.

5. *Lime water* and all the soluble *calcium salts*, including *solution of calcium sulphate*, produce in even highly dilute solutions of oxalic acid or of oxalates of the alkalies, white finely pulverulent precipitates of CALCIUM OXALATE, $Ca C_2 O_4 + H_2 O$, and sometimes $Ca C_2 O_4 + 3 H_2 O$, which dissolve readily in hydrochloric acid and in nitric acid, but are nearly insoluble in oxalic acid and in acetic acid, and practically insoluble in water. The presence of ammonium salts does not interfere with the formation of these precipitates. Addition of ammonia considerably promotes the precipitation of free oxalic acid by calcium salts. In highly dilute solutions the precipitate is only formed after some time.

6. If oxalic acid or an oxalate, in the dry state, is heated with an excess of *concentrated sulphuric acid*, it is decomposed into CARBON MONOXIDE and CARBON DIOXIDE, with formation of water or a sulphate if a base be present, the two gases escaping with effervescence, *e.g.*, $C_2 H_2 O_4 = C O + C O_2 + H_2 O$. If the quantity operated upon is not too minute, the carbon monoxide may be kindled; it burns with a blue flame.

Should the sulphuric acid acquire a dark color in this reaction, this is a proof that the oxalic acid contained some organic substance in admixture.

7. If oxalic acid or an oxalate is mixed with finely pulverized *manganese dioxide* (which must be free from carbonates), a little water added and a few drops of sulphuric acid, a lively effervescence ensues, caused by escaping CARBON DIOXIDE, $C_2 H_2 O_4 + Mn O_2 + H_2 S O_4 = 2 C O_2 + 2 H_2 O + Mn S O_4$.

8. If oxalates of alkali-earth metals are boiled with a concentrated solution of *sodium carbonate*, and filtered, sodium oxalate is obtained in the filtrate, whilst the precipitate contains the base as carbonate. With oxalates of heavy metals, this operation is not always sure to attain the desired object, as many of these oxalates, *e.g.*, nickel, ferric and chromic oxalates, will partially dissolve in the alkaline fluid, with formation of double salts. Metals of this kind should therefore be separated as sulphides.

§ 146.

d. HYDROFLUORIC ACID, H F. (F. 19.)

1. HYDROFLUORIC ACID is a colorless corrosive gas, which fumes in the air, and is freely absorbed by water. Aqueous hydrofluoric acid is distinguished from all other acids by the property of dissolving crystallized silicic oxide, and also the silicates which are insoluble in hydrochloric acid. Hydrofluosilicic acid and water are formed in the process of solution, $Si O_2 + 6 H F = H_2 Si F_6 + 2 H_2 O$. With metallic oxides and hydroxides hydrofluoric acid forms metallic fluorides and water.

2. The FLUORIDES of the alkali metals are soluble in water; the solutions have an alkaline reaction. The fluorides of the metals of the alkali-earths are either insoluble or very difficultly soluble in water. Aluminium fluoride is readily soluble. Most of the fluorides of the heavy metals are very sparingly soluble in water, as the fluorides of copper, lead and zinc; many others dissolve in water without difficulty, as the ferric, stannous and mercurous fluorides. Many of the fluorides insoluble or difficultly soluble in water dissolve in hydrofluoric acid; others do not. Most of the fluorides bear ignition in a crucible without suffering decomposition.

3. *Barium chloride* precipitates aqueous solutions of hydrofluoric acid, but much more completely solutions of fluorides of the alkalies.

The bulky white precipitate of BARIUM FLUORIDE ($Ba F_2$) is almost absolutely insoluble in water, but dissolves in large quantities of hydrochloric acid or nitric acid, from which solutions ammonia fails to precipitate it, or throws it down only very incompletely, owing to the dissolving action of the ammonium salts.

4. *Calcium chloride* produces in aqueous solutions of hydrofluoric acid or of fluorides a gelatinous precipitate of CALCIUM FLUORIDE ($Ca F_2$), which is so transparent as at first to induce the belief that the fluid has remained perfectly clear.

Addition of ammonia promotes the complete separation of the precipitate. The precipitate is practically insoluble in water, and only very slightly soluble in hydrochloric acid and nitric acid in the cold; it dissolves somewhat more largely upon boiling with hydrochloric acid. Ammonia produces no precipitate in the solution, or only a very trifling one, as the ammonium salt formed retains it in solution. Calcium fluoride is scarcely more soluble in hydrofluoric acid than in water. It is insoluble in alkaline fluids.

5. If a finely pulverized fluoride, no matter whether soluble

or insoluble, is treated in a platinum crucible with just enough *concentrated sulphuric acid* to make it into a thin paste, the crucible covered with the convex face of a watch-glass of hard glass coated with beeswax, which has been removed again in some places by tracing lines in it with a pointed piece of wood, the hollow of the glass filled with water, and the crucible gently heated for the space of half an hour or an hour, the exposed lines will, upon the removal of the wax, be found more or less deeply ETCHED into the glass. (The coating is made by heating the glass cautiously, putting a small piece of wax upon the convex face, and spreading the wax equally as it melts. The wax is removed by heating the glass gently, and wiping with paper.) If the quantity of hydrofluoric acid disengaged by the sulphuric acid was very minute, the etching is often invisible upon the removal of the wax; it will, however, in such cases appear when the glass is breathed upon. This appearance of the etched lines is owing to the unequal capacity of condensing water which the etched and the untouched parts of the plate respectively possess. The impressions which thus appear upon breathing on the glass may, however, owe their origin to other causes; therefore, though their non-appearance may be held as a proof of the absence of fluorine, their appearance is not a positive proof of the presence of that element. At all events, they ought only to be considered of value where they can be developed again after the glass has been properly washed with water, dried, and wiped.*

This reaction fails if there is too much silicic oxide or of a silicate present, or if the substance is not decomposed by sulphuric acid. In such cases one of the two following methods is resorted to, according to circumstances.

6. If we have to deal with a fluoride *decomposable by sulphuric acid*, but mixed with a large proportion of silicic oxide or of a silicate, the fluorine in it may be detected by heating the mixture in a test-tube with *concentrated sulphuric acid*, as FLUOSILICIC GAS (or SILICON FLUORIDE, SiF_4) is evolved in this process, which forms dense white fumes in moist air. If the gas is conducted into

* J. NICKLÉS states that etchings on glass may be obtained with all kinds of sulphuric acid, and, in fact, with all acids suited to effect evolution of hydrofluoric acid. I have tried watch-glasses of Bohemian glass with sulphuric and other acids, but could get no etchings in confirmation of this statement. Still, proper caution demands that before using the sulphuric acid, it should first be positively ascertained that its fumes will not etch glass. Should the sulphuric acid contain hydrofluoric acid, the latter may be easily removed by diluting with an equal volume of water and evaporating in a platinum dish to the original strength.

water through a bent tube moistened inside, the latter has its transparency more or less impaired, owing to the separation of silicic acid. If the quantity operated upon is rather considerable, silicic acid separates in the water, and the fluid is rendered acid by hydrofluosilicic acid. Compare § 146, 1.

This process is best applied for the detection of small quantities of fluorine as follows: Heat the substance with concentrated sulphuric acid in a small flask closed with a cork with double perforation, bearing two tubes, one of which reaches to the bottom of the flask, whilst the other terminates immediately under the cork. Conduct through the longer tube a slow stream of dry air into the flask, and conduct this, upon its reissuing through the other tube, into a U tube containing a little dilute ammonia, and connected at the other end with an aspirator. The silicon fluoride which escapes with the air, decomposes with the ammonia, more particularly upon the application of a gentle heat towards the end of the process, ammonium fluoride and silicic acid being formed. Filter, evaporate in a platinum crucible to dryness, and examine the residue by 5. For more difficultly decomposable substances potassium disulphate is used instead of sulphuric acid, and the mixture, to which some marble is added (to insure a continuous slight evolution of gas), heated to fusion, and kept in that state for some time.

7. Silicates, whether decomposable or not by sulphuric acid, are first fused with four parts of sodium carbonate. The fused mass is treated with water, the solution filtered, the filtrate concentrated by evaporation, allowed to cool, transferred to a platinum vessel, hydrochloric acid added to feebly acid reaction, and the fluid allowed to stand until the carbon dioxide has escaped. It is then supersaturated with ammonia, heated, filtered into a bottle, calcium chloride added to the still hot fluid, the bottle closed, and allowed to stand at rest. If a precipitate separates after some time it is collected on a filter, dried, and examined by the method described in 5 (H. Rose).

8. Minute quantities of metallic fluorides in minerals, slags, etc., may also be readily detected by means of the *blowpipe*. Bend a piece of platinum foil, and insert it in a glass tube as shown in Fig. 42, introduce the finely triturated substance mixed with fused and powdered sodium metaphosphate, and let the blowpipe flame play upon it so that the products of combustion may pass into the tube. A metallic fluoride treated in this way yields hydrofluoric acid gas, which betrays its presence by its pungent odor, the dimming of the glass tube (which becomes perceptible only after cleaning and drying), and the yellow tint which the acid air issuing from the tube imparts to a moist slip of Brazil-wood paper* (Berzelius, Smithson). When silicates containing metallic fluorides are treated in this manner, gaseous silicon fluoride is formed, which also colors yellow a

Fig. 42.

* Prepared by moistening slips of fine printing-paper with decoction of Brazil-wood.

moist slip of Brazil-wood paper inserted in the tube, and leads to silicic acid being deposited within the tube. After washing and drying the tube, it appears here and there dimmed. A small quantity of a fluoride present in a mineral containing water may generally be detected by heating the substance by itself in a glass tube sealed at one end and inserting a slip of Brazil-wood paper in the tube ; under the circumstance the paper will usually turn yellow (BERZELIUS).

§ 147.

Recapitulation and remarks.—The barium compounds of the acids of the third division are dissolved by hydrochloric acid, apparently without decomposition ; alkalies therefore reprecipitate them unaltered, by neutralizing the hydrochloric acid. The barium compounds of the acids of the first division show, however, the same deportment ; these acids must, therefore, if present, be removed before any conclusion regarding the presence of phosphoric acid, boric acid, oxalic acid, or hydrofluoric acid, can be drawn from the reprecipitation of a barium salt by alkalies. But even leaving this point altogether out of the question, no great value is to be placed on this reaction, not even so far as the simple detection of these acids is concerned, and far less still as regards their separation from other acids, since ammonia fails to reprecipitate from hydrochloric acid solutions the barium salts in question, and more particularly barium borate and barium fluoride, if the solution contains any considerable proportion of free acid or of an ammonium salt.

Boric acid is well characterized by the coloration which it imparts to the flame of alcohol, and also by its action on turmeric paper. The latter reaction is more particularly suited for the detection of very minute traces. Heavy metals, if present, are most conveniently removed first by hydrosulphuric acid or ammonium sulphide. Before proceeding to concentrate dilute solutions of boric acid, the acid must be combined with an alkali, otherwise a large portion of it will volatilize with the aqueous vapors. Small quantities of boric acid may also be safely and easily detected by the spectroscope.

The detection of *phosphoric acid* in compounds soluble in water is not difficult ; the reaction with magnesium sulphate, etc., is the best adapted for the purpose. The detection of phosphoric acid in insoluble compounds cannot be effected by means of magnesium solution. Ferric chloride (§ 142, 9) is well suited for the detection of phosphoric acid in its salts with the alkali-earth metals, and more particularly for the separation of the acid from the alkali-earth metals ; the nitric acid solution of ammonium molybdate is more espe-

cially adapted to effect the detection of phosphoric acid in presence of aluminium and iron. I must repeat again that both these reactions demand the *strictest* attention to the directions given. If present in combination with oxides of the fourth, fifth, or sixth group, phosphoric acid may be separated by the method given § 142, 11, or by precipitating the bases with hydrosulphuric acid or ammonium sulphide.

Oxalic acid may always be easily detected in aqueous solutions of oxalates of the alkalies, by solution of calcium sulphate. The formation of a finely pulverulent precipitate, insoluble in acetic acid, leaves hardly a doubt on the point, as racemic acid alone, which occurs so very rarely, gives the same reaction. In case of doubt the calcium oxalate may be readily distinguished from the racemate, by simple ignition, with exclusion of air, as the decomposed racemate leaves a considerable proportion of charcoal behind; the racemate dissolves moreover in cold solution of potassa or soda, in which calcium oxalate is insoluble. The deportment of the oxalates with sulphuric acid, or with manganese dioxide and sulphuric acid, affords also sufficient means to confirm the results of other tests. In insoluble salts the oxalic acid is detected most safely by decomposing them by boiling with solution of sodium carbonate, or by hydrosulphuric acid or ammonium sulphide (§ 145, 8). I must finally also call attention here to the fact that there are certain soluble oxalates which are not precipitated by calcium salts; these are more particularly chromic oxalate and ferric oxalate. Their non-precipitation is owing to the circumstance that these salts form soluble double salts with calcium oxalate.

Hydrofluoric acid is readily detected in salts decomposable by sulphuric acid; only it must be borne in mind that an over-large proportion of sulphuric acid impedes the free evolution of hydrofluoric gas, and thus impairs the delicacy of the reaction; also that the glass cannot be distinctly etched if, instead of hydrofluoric acid, silicon fluoride alone is evolved; and, therefore, in the case of compounds abounding in silicon, the safer way is to try, besides the reaction given § 146, 5, also the one given in 6. In silicates which are not decomposed by sulphuric acid, the presence of fluorine is often overlooked, because the analyst omits to examine the compound carefully by the method given in 7.

§ 148.

PHOSPHOROUS ACID, $H_3 P O_3$.

Phosphorous oxide ($P_2 O_3$) is a white powder, which admits of sublimation, and burns when heated in the air. It forms with a small proportion of water a thickish fluid, which by long standing yields crystals of phosphorous acid. Heat decomposes phosphorous acid into phosphoric acid, and phosphoretted hydrogen gas, which does not spontaneously take fire. It freely dissolves in water. Of the salts those with alkali base are readily soluble in water, all the others sparingly soluble; the latter dissolve in dilute acids. All the salts are decomposed by ignition into phosphates, which are left behind, and hydrogen, or a mixture of hydrogen and phosphoretted hydrogen, which escapes. With *silver nitrate* separation of metallic silver takes place, more especially upon addition of ammonia and application of heat; with *mercurous nitrate*, under the same circumstances, separation of metallic mercury. From *mercuric chloride* in excess phosphorous acid throws down mercurous chloride after some time, more rapidly upon heating. *Barium chloride* and *calcium chloride* produce in not over-dilute solutions of phosphorous acid, upon addition of ammonia, white precipitates soluble in acetic acid. A mixture of magnesium sulphate, ammonium chloride, and ammonia will precipitate only rather concentrated solutions. *Lead acetate* throws down white lead phosphite, insoluble in acetic acid. By heating to boiling with *sulphurous acid* in excess, phosphoric acid is formed, attended by separation of sulphur. In contact with *zinc* and *dilute sulphuric acid* phosphorous acid gives a mixture of hydrogen with phosphoretted hydrogen, which accordingly fumes in the air, burns with an emerald-green color, and precipitates silver and silver phosphide from solution of silver nitrate.

Fourth Division of the First Group of the Inorganic Acids.

§ 149.

a. CARBON, C. 12, AND CARBONIC ACID, $H_2 CO_3$.

1. CARBON is a solid tasteless and inodorous body. The very highest degrees of heat alone can effect its fusion and volatilization. All carbon is combustible and yields carbon dioxide, when burnt with a sufficient supply of oxygen or atmospheric air. In the diamond the carbon is crystallized, transparent, pellucid, exceedingly hard, difficultly combustible; in the form of graphite it is opaque, blackish-gray, soft, greasy to the touch, difficultly combustible, and stains the fingers; as charcoal, produced by the decomposition of organic matter, it is black, opaque, non-crystalline—sometimes dense, shining, and difficultly combustible, and sometimes porous, dull, and readily combustible.

2. CARBON DIOXIDE OR CARBONIC ANHYDRIDE, $C O_2$, at the common temperature and common atmospheric pressure, is a colorless gas of far higher specific gravity than atmospheric air, so that it may be poured from one vessel into another.

It is inodorous, has a sourish taste, and reddens moist litmus paper; but the red tint disappears again upon drying. Carbon dioxide is readily absorbed by solution of soda, forming a carbonate; it dissolves pretty copiously in water, and the solution may be assumed to contain CARBONIC ACID, H_2CO_3 ($= CO_2 + H_2O$), although this body has not been isolated.*

3. The AQUEOUS SOLUTION OF CARBONIC ACID has a feebly acid and pungent taste; it transiently imparts a red tint to litmus paper, and colors solution of litmus wine-red; it loses carbon dioxide when shaken with air in a half-filled bottle, and more completely still upon application of heat. Some of the CARBONATES lose carbon dioxide by ignition; most of them are white or colorless. Of the normal carbonates only those with alkali base are soluble in water. The solutions manifest a very strong alkaline reaction; most of the carbonates insoluble in water dissolve in aqueous carbonic acid.

4. The carbonates are decomposed by all free *acids* soluble in water, with the exception of hydrocyanic acid and hydrosulphuric acid. Most carbonates are decomposed in the cold, but several (magnesite, for instance) require heat. The decomposition is attended with EFFERVESCENCE, carbon dioxide being disengaged as a colorless and inodorous gas, which transiently imparts a reddish tint to moist litmus paper. It is necessary to apply the decomposing acid in excess, especially when operating upon carbonates with alkali base, since the formation of hydrogen carbonates will frequently prevent effervescence if too little of the decomposing acid be added. Substances which it is intended to test for carbonic acid should first be heated with a little water, to prevent any mistake which might arise from the escape of air-bubbles upon treating the dry substances with the acid. Where there is reason to apprehend loss of carbonic acid upon boiling with water, lime water should be used instead of pure water. If you wish to prove that the escaping gas is really carbon dioxide, dip a glass rod in baryta water and hold it inside the test-tube near the fluid; a white pellicle will form on the baryta water, as is explained in 5.

* Carbonic acid, $CO<^{OH}_{OH}$; Sodium carbonate (normal), $CO<^{ONa}_{ONa}$;

Hydrogen sodium carbonate (acid) $CO<^{OH}_{ONa}$; Barium carbonate, $CO<^{O}_{O}>Ba$.

5. *Lime water* and *baryta water*, brought into contact with carbon dioxide, carbonic acid, or with soluble carbonates, produce white precipitates of normal CALCIUM CARBONATE, $CaCO_3$, or BARIUM CARBONATE, $BaCO_3$. In testing for free carbonic acid the reagents ought always to be added in excess, as the carbonates of the alkali earths are soluble in aqueous carbonic acid. The precipitates dissolve in acids with effervescence, and are not reprecipitated from such solutions by ammonia, after the complete expulsion of the carbonic acid by ebullition.

As lime water dissolves very minute quantities of calcium carbonate, the detection of exceedingly minute traces of carbonic acid requires the use of a lime water saturated with calcium carbonate by long digestion therewith (WELTER, BERTHOLLET).

6. *Calcium chloride* and *barium chloride* immediately produce in solutions of normal alkali carbonates, precipitates of CALCIUM CARBONATE or of BARIUM CARBONATE; in dilute solutions of acid carbonates these precipitates are formed only upon ebullition; with aqueous carbonic acid these reagents give no precipitate.

§ 150.

b. SILICIC ACID, $Si(OH)_4$ (Si. 28).

1. SILICIC OXIDE or SILICA is colorless or white, in the common blowpipe flame unalterable and infusible. It fuses in the flame of the oxyhydrogen blowpipe. It is met with in the crystalline state (quartz, tridymite), and amorphous. It is insoluble in water and acids (with the exception of hydrofluoric acid, which dissolves the amorphous variety easily, the crystalline varieties with more difficulty). The amorphous silicic oxide dissolves in hot aqueous solutions of potassa and soda and their carbonates; but the crystallized silicic oxide is insoluble or nearly so in these fluids. If either of the two is fused with excess of a caustic alkali or alkali carbonate, a basic silicate of the alkali is obtained which is soluble in water. The SILICATES with alkali base alone are soluble in water.

2. The solutions of the alkaline silicates are decomposed by all *acids*. If a large proportion of hydrochloric acid is

added at once to even concentrated solutions of alkali silicates the separated silicic acid remains in solution, probably as the normal acid, $Si(OH)_4$; but if the hydrochloric acid is added gradually drop by drop, whilst stirring the fluid, the greater part of the silicic acid separates in a gelatinous form. The more dilute the fluid, the more silicic acid remains in solution, and in highly dilute solutions no precipitate is formed. If the solution of an alkali silicate, mixed with hydrochloric or nitric acid in excess, *is evaporated to dryness* silicic acid separates in proportion as the acid escapes; upon treating the residue with hydrochloric acid and water the silicic acid remains as an insoluble white powder.* Ammonium chloride produces in not over-dilute solutions of alkali silicates precipitates of silicic acid (containing alkali). Heating promotes the separation. Silicic acid is readily soluble in hot solution of potassa or soda and in hot solutions of normal potassium and sodium carbonates.

3. Some of the silicates insoluble in water are decomposed by hydrochloric acid or nitric acid, others are not affected by these acids, even upon boiling. In the decomposition of the former the greater portion of the silicic acid separates, usually in the gelatinous, more rarely in the pulverulent form. To effect the complete separation of the silicic acid, the hydrochloric acid solution, with the precipitated silicic acid suspended in it, is evaporated to dryness, the residue heated with stirring, at a uniform temperature, somewhat above the boiling point of water for 15 minutes, then moistened with hydrochloric acid, heated with water, and the fluid containing the bases filtered from the residuary insoluble silicic acid.

Of the silicates not decomposed by hydrochloric acid many, *e.g.* kaolin, are completely decomposed by heating with a mixture of 8 parts of strong sulphuric acid and 3 parts of water, the silicic acid being separated in the pulverulent form; many others are acted upon to some extent by this reagent. Silicates not decomposable by boiling with hydrochloric or sulphuric acid in the open air, may generally be completely decomposed by heating in a state of fine powder with the acids in sealed glass tubes at 200°–210° in an air or paraffin bath.

4. If a silicate, reduced to a fine powder, is fused with 4 parts of *sodium carbonate*, and the fused mass is then boiled

* The gelatinous silicic acid, and the dried "silica" are probably anhydroacids, analogous to pyrophosphoric acid and metaphosphoric acid.

with water, the greater part of the silicic acid dissolves as sodium silicate, whilst alkali earth and earth metals (with the exception of aluminium and beryllium, which pass more or less completely into the solution), and heavy metals are left undissolved as carbonates or oxides. If the fused mass is treated with water, then, without previous filtration, hydrochloric or nitric acid added to strongly acid reaction, and the fluid evaporated as directed in 3, the silicic acid is left undissolved, whilst the bases are dissolved.

5. If an insoluble silicate containing alkali metals is mixed in the state of powder with 3 times its weight of precipitated *calcium carbonate* and one-half its weight of *ammonium chloride*, and the mixture is heated in a platinum crucible for half an hour to redness, too high a heat being avoided, a somewhat sintered mass is obtained, which, on being digested in hot water, falls to powder, and yields a solution containing, besides calcium chloride and hydroxide, all the alkalies of the silicate, in the form of chlorides (J. LAWRENCE SMITH).

6. If *hydrofluoric acid*, in concentrated aqueous solution or in the gaseous state, is made to act upon silicic oxide, fluosilicic gas escapes ($SiO_2 + 4HF = SiF_4 + 2H_2O$); dilute acid dissolves silica to hydrofluosilicic acid ($SiO_2 + 6HF = H_2SiF_6 + 2H_2O$). Hydrofluoric acid acting upon silicates gives rise to the formation of silicofluorides ($CaSiO_3 + 6HF = CaSiF_6 + 3H_2O$, which by heating with hydrated sulphuric acid are changed to sulphates, with evolution of hydrofluoric and fluosilicic gases. If the powdered silicate is mixed with 3 parts of ammonium fluoride, or 5 parts of calcium fluoride in powder, the mixture made into paste with concentrated sulphuric acid, and heat applied (best in the open air) until no more fumes escape, the whole of the silicic acid present volatilizes as fluosilicic gas. The bases present are found in the residue as sulphates, mixed, if calcium fluoride was used, with calcium sulphate.

7. On mixing 1 part of finely powdered silica, or a silicate, with 2 parts of powdered cryolite or fluor spar (free from silica), and 4 or 5 parts of concentrated sulphuric acid, heating the mixture moderately in a platinum crucible, but not allowing it to spurt, and then holding close over the surface the loop of a stout platinum wire which has been freshly ignited, and now contains a drop of water, a pellicle of silicic acid will soon form on the latter from decomposition of the escaping silicon fluoride (BARFOED).

8. If silicic oxide or a silicate is fused with a small proportion of *sodium carbonate* in the loop of a platinum wire FROTHING is observed in the bead owing to the evolution of carbon dioxide. The bead obtained with pure silicic acid, or silicic oxide, is always clear when hot; with silicates when they are rich in silicic acid (as the felspathic rocks), the bead is also clear, otherwise it is opaque. The clearness of the cold bead depends upon the proportion between silicic acid, sodium and other bases.

9. *Sodium metaphosphate*, in a state of fusion, fails nearly altogether to dissolve silicic oxide. If, therefore, silicic acid or a silicate is fused, in small fragments, with hydrogen ammonium sodium phosphate on a platinum wire, the bases are dissolved, whilst silicic oxide separates and floats about in a clear bead as a more or less translucent mass, exhibiting the shape of the fragment of substance used.

§ 151.

Recapitulation and remarks.—Carbon dioxide or free *carbonic acid* is readily known by the reaction with lime water; the carbonates are easily detected by the evolution of an inodorous gas, when they are treated with acids. When operating upon compounds which evolve other gases besides carbon dioxide, the gas is to be tested with lime water or baryta water. *Silicic acid*, both in the free state and in silicates, may usually be readily detected by the reaction with sodium metaphosphate. It differs moreover from all other bodies in the form in which it is always obtained in analyses, by its insolubility in acids (except hydrofluoric acid), and in fusing potassium disulphate, and its solubility in boiling solutions of alkalies and alkali carbonates; and from many bodies (especially from titanic oxide), by completely volatilizing upon repeated evaporation in a platinum dish, with hydrofluoric acid (or ammonium fluoride) and sulphuric acid.

Second Group.

ACIDS WHICH ARE PRECIPITATED BY SILVER NITRATE, BUT NOT BY BARIUM CHLORIDE: *Hydrochloric Acid*, *Hydrobromic Acid*, *Hydriodic Acid*, *Hydrocyanic Acid*, *Hydroferro-* and *Hydroferricyanic Acid*, *Hydrosulphuric Acid* (Nitrous Acid, Hypochlorous Acid, Chlorous Acid, Hypophosphorous Acid).

The silver compounds corresponding to the *halogen* and *sulphur acids* of this group, are insoluble in dilute nitric acid. These acids decompose with metallic oxides and hydroxides, the metals combining with the chlorine, bromine, iodine, cyanogen, or sulphur, whilst the oxygen of the metallic oxide, or the hydroxyl of the hydroxide, forms water with the hydrogen of the acid.

§ 152.

a. Chlorine, Cl. 35.5, and Hydrochloric Acid, H Cl.

1. Chlorine is a heavy yellowish-green gas of a disagreeable and suffocating odor, which has a most injurious action upon the respiratory organs; it destroys many vegetable colors (litmus, indigo-blue, etc.); it is not inflammable, and supports the combustion of few bodies only. Minutely divided antimony, tin, etc., spontaneously ignite in it, and are converted into chlorides. It dissolves pretty freely in water; the chlorine water formed has a faint yellowish-green color, smells strongly of the gas, bleaches vegetable colors, is decomposed by the action of light (§ 31), and loses its smell when shaken with mercury, the latter being converted into a mixture of mercurous chloride and metal. Small quantities of free chlorine may be readily detected in a fluid by the red color imparted to a mixture of potassium sulphocyanate and a ferrous salt, or—in the absence of nitrous acid—by the blue color imparted to a mixture of starch paste and potassium iodide (see § 154, 9).

2. Hydrochloric acid, at the common temperature and common atmospheric pressure, is a colorless gas, which forms dense fumes in the air, is suffocating and very irritating, and dissolves in water with exceeding facility. The concentrated solution (fuming hydrochloric acid) loses a large portion of its gas upon heating.

3. The normal metallic chlorides are readily soluble in water, with the exception of lead, silver and mercurous chlorides; most of the chlorides are white or colorless. Many of them volatilize at a high temperature, without suffering decomposition; others are decomposed upon ignition, and many of them are fixed at a moderate red heat.

4. *Silver nitrate* produces in even highly dilute solutions of free hydrochloric acid or of metallic chlorides white precipitates of argentic chloride, Ag Cl, which upon exposure to light change first to violet, then to black by reduction to argentous chloride, Ag_2Cl; they are insoluble in dilute nitric acid, but dissolve readily in ammonia as well as in potassium cyanide, and fuse without decomposition when heated. (Compare § 115, 7.) Placed in contact with metallic zinc and water slightly acidulated with sulphuric acid, argentic chloride is decomposed; soluble zinc chloride and metallic silver being formed.

5. *Mercurous nitrate and lead acetate* produce in solutions containing free hydrochloric acid or metallic chlorides precipitates of mercurous chloride, Hg_2Cl_2, and lead chloride, $PbCl_2$. For the properties of these precipitates see § 116, 6, and § 117, 7.

6. If hydrochloric acid is heated with *manganese dioxide*, or a chloride with *manganese dioxide* and *sulphuric acid*, chlorine is evolved, which may be readily recognized by its odor, its yellowish-green color, and its bleaching action upon vegetable colors. The best way of testing the latter is to expose to the gas a moist slip of litmus paper, or of paper colored with solution of indigo.

7. If a metallic chloride is triturated with *potassium dichromate*, the dry mixture treated with *concentrated sulphuric acid* in a tubulated retort, and a gentle heat applied, the deep brownish-red gas of CHROMIC OXYCHLORIDE, CrO_2Cl_2 ("CHLOROCHROMIC ACID"), is copiously evolved, which condenses into a fluid of the same color, and passes into the receiver. If this distillate is mixed with ammonia in excess, a yellow-colored liquid is produced, from the formation of ammonium chromate, $CrO_2Cl_2 + 4NH_3 + 2H_2O = CrO_4(NH_4)_2 + 2NH_4Cl$. Upon addition of an acid the color of the solution changes to a reddish-yellow, owing to the formation of ammonium dichromate.

8. In the metallic chlorides insoluble in water and nitric acid the chlorine is detected by fusing them with *sodium carbonate*, and treating the fused mass with water, which will dissolve, besides the excess of the sodium carbonate, the sodium chloride formed in the process.

9. If in a bead of *sodium metaphosphate* on a platinum wire, *cupric oxide* be dissolved in the outer blowpipe flame in sufficient quantity to make the mass nearly opaque, a trace of a substance containing chlorine added to it while still in fusion, and the bead then exposed to the reducing flame, a fine BLUE-COLORED flame, inclining to PURPLE, will be seen encircling it so long as chlorine is present (BERZELIUS). With regard to the spectrum of copper chloride, compare § 157.

§ 153.

b. BROMINE, Br. 80, AND HYDROBROMIC ACID, H Br.

1. BROMINE is a heavy reddish-brown fluid of a very disagreeable chlorine-like odor; it boils at 63°, and volatilizes rapidly even at the common temperature. The vapor is brownish-red. Bromine bleaches vegetable colors like chlorine; it is pretty soluble in water, but dissolves more readily in alcohol, and very freely in ether. The solutions are yellowish-red.

2. HYDROBROMIC ACID GAS, its AQUEOUS SOLUTION and the METALLIC BROMIDES offer in their general deportment a great analogy to the corresponding chlorides.

3. *Silver nitrate* produces in aqueous solutions of hydrobromic acid or of bromides a yellowish-white precipitate of SILVER BROMIDE, Ag Br, which changes to gray upon exposure to light; this precipitate is insoluble in dilute nitric acid, and somewhat sparingly soluble in ammonia, but dissolves with facility in potassium cyanide. With metallic zinc and

water acidulated with sulphuric acid it yields soluble zinc bromide and metallic silver.

4. *Palladious nitrate*, but not palladious chloride, produces in neutral solutions of metallic bromides a reddish-brown precipitate of PALLADIOUS BROMIDE. In concentrated solutions this precipitate is formed immediately; in dilute solutions it makes its appearance only after standing some time.

5. *Nitric acid* decomposes hydrobromic acid and the bromides, with the exception of silver and mercury bromides, upon the application of heat, and liberates the bromine, by oxidizing the hydrogen or the metal. In the case of a solution, the liberated bromine colors it yellow or yellowish-red. With bromides in the solid state or in concentrated solution, brownish-red (if diluted, brownish-yellow) vapors of bromine gas escape at the same time, which, if evolved in sufficient quantity, condense in the cold part of the test-tube to small drops. In the cold, nitric acid, even the red fuming, fails to liberate the bromine in very dilute solutions of bromides, nor is it liberated by solution of nitro-sulphonic acid,* or by hydrochloric acid and potassium nitrite.

6. *Chlorine*, in the *gaseous* state or in *solution*, immediately liberates bromine in the solutions of its compounds; the fluid assuming a yellowish-red tint if the quantity of the bromine present is not too minute. A large excess of chlorine must be avoided, since this will cause formation of bromine chloride, which will destroy the color wholly or nearly so. This reaction is made much more delicate by addition of a fluid which dissolves bromine and does not mix with water, as carbon disulphide or chloroform. Mix the neutral or feebly acid solution in a test-tube with a little of one of these fluids, sufficient to form a large drop at the bottom, then add dilute chlorine water drop by drop, and shake the tube. With appreciable quantities of bromine, *e.g.*, 1 part in 1,000 parts of water, the drop at the bottom acquires a reddish-yellow tint; with very minute quantities (1 part of bromine in 30,000 parts of water), a pale yellow tint, which, however, is still distinctly discernible. A large excess of chlorine water must be avoided in this experiment also, and it must always be ascertained first whether the chlorine water, mixed with a large quantity of water and some carbon disulphide or chloroform, and shaken, will leave these reagents quite uncolored. If not, the chlorine water is not suited for the intended purpose. If the solution of bromine in carbon disulphide or chloroform is mixed with some solution of potassa, the mixture shaken, and heat applied, the yellow

* See the first note, p. 257.

color disappears, and the solution now contains potassium bromide and bromate. By evaporation and ignition the potassium bromate is converted into potassium bromide, and the ignited mass may then be further tested as directed in 7.

7. If bromides are heated with *manganese dioxide* and *sulphuric acid*, BROWNISH-RED VAPORS OF BROMINE are evolved. Presence of chlorides in large proportion is not favorable to the reaction and requires addition of some water, and the sulphuric acid to be added gradually in *very small* quantities. If the bromine is present only in very minute quantity, the color of these vapors is not visible. But if the mixture is heated in a small retort, and the vapors are transmitted through a long glass condenser, the color of the bromine may generally be seen by looking lengthwise through the tube, and the first drops of the distillate are also colored yellow. The first vapors and the first drops of the distillate should be received in a test-tube containing some starch moistened with water ; since

8. If moistened *starch** is brought into contact with free bromine, more especially in form of vapor, YELLOW BROMIZED STARCH is formed. The coloration is not always instantaneous. The reaction is rendered most delicate by sealing the test-tube which contains the moistened starch and the first drops of the distillate from 7, and then cautiously inverting it, so as to cause the moist starch to occupy the upper part of the tube whilst the fluid occupies the bottom. The presence of even the slightest trace of bromine will now, in the course of from twelve to twenty-four hours, impart a yellow tint to the starch, which, however, after some time, will again disappear. The reaction may be called forth in a simple manner, almost with the same degree of delicacy, by gently heating the fluid containing free bromine, or also the original mixture of bromide, manganese dioxide, and sulphuric acid, in a very small beaker, covered with a watch-glass with a slip of paper attached to the lower side, moistened with starch paste, and sprinkled with starch powder.

9. If sulphuric acid is poured over a mixture of a bromide with *potassium dichromate*, and heat is then applied, a brownish-red gas is evolved, exactly as in the case of chlorides. But this gas consists of pure BROMINE, and therefore the fluid passing over does not turn yellow, but becomes colorless upon supersaturation with ammonia.

10. If a solution of hydrobromic acid or a bromide is mixed with a little *hydrochlorauric acid*, a straw color or dark orange color is produced from the formation of HYDROBROMAURIC ACID. If iodine is present it must be removed before the solution of gold is added (BILL).

11. In the metallic bromides, which are insoluble in water and nitric acid, the bromine is detected in the same way as the chlorine in the corresponding chlorides.

12. If a substance containing bromine is added to a *sodium metaphosphate bead saturated with cupric oxide*, and the bead is then ignited in the inner blowpipe flame, the flame is colored BLUE, inclining to GREEN, more particularly at the edges (BERZELIUS). With regard to the spectrum of copper bromide see § 157.

* [See that the starch is not of the kind which, *as powder*, is made yellow by iodine. Such starch, boiled to a paste, reacts blue with iodine.—NÄGELI.]

§ 154.

c. Iodine, I. 127, and Hydriodic Acid, H I.

1. Iodine is a solid soft body of a peculiarly disagreeable odor. It is generally seen in the form of black, shining, crystalline scales. It fuses at a gentle heat; at a somewhat higher temperature it is converted into vapor, which has a beautiful violet-blue color, and condenses upon cooling to a black sublimate. It is very sparingly soluble in water, but readily in alcohol and ether, as well as in solution of potassium iodide. The aqueous solution is light brown, the alcoholic, ethereal, and potassium iodide solutions are deep red-brown. Iodine destroys vegetable colors only slowly and imperfectly; it stains the skin brown.

Crystals of iodine, its vapor and its solutions (best the aqueous) give to *moist starch powder*, sometimes a yellow, most usually a purple or blue color, with *starch paste* always an intensely purple or deep blue. The color of *iodized starch* is destroyed by alkalies, by chlorine and bromine, and by sulphurous acid and other reducing agents.

2. Hydriodic acid gas resembles hydrochloric and hydrobromic acid gas; it dissolves copiously in water. The colorless solution of hydriodic acid turns speedily to a reddish brown in contact with the air, water being formed, and a solution of iodine in hydriodic acid.

3. The iodides also correspond in many respects with the chlorides. Of the iodides of the heavy metals, however, many more are insoluble in water than is the case with the corresponding chlorides. Many iodides have characteristic colors, *e.g.*, lead iodide, mercurous iodide and mercuric iodide.

4. *Silver nitrate* produces in aqueous solutions of hydriodic acid and of iodides yellowish-white precipitates of argentic iodide, Ag I, which blacken on exposure to light; these precipitates are insoluble in dilute nitric acid, and *very sparingly soluble in ammonia*, but dissolve readily in potassium cyanide. They react with metallic zinc like silver bromide.

5. *Palladious chloride* and *palladious nitrate* produce even in very dilute solutions of hydriodic acid or metallic iodides, a brownish-black precipitate of palladious iodide ($Pd I_2$), which dissolves to a trifling extent in saline solutions (sodium chloride, magnesium chloride, etc.), but is insoluble or nearly so in dilute cold hydrochloric and nitric acids.

6. A solution of 1 part of *cupric sulphate* and 2½ parts of *ferrous sulphate* throws down from neutral aqueous solutions of the iodides cuprous iodide ($Cu_2 I_2$), in the form of a dirty white precipitate. The addition of ammonia promotes the complete precipitation of the iodine. Chlorides and bromides are not precipitated by this reagent. Instead of using the above mixture of sulphates, cupric sulphate alone may be added, and afterwards enough sulphurous acid to remove the brown color produced by separated iodine.

7. Pure *nitric acid*, free from nitrous acid, decomposes hydriodic acid or iodides only when acting upon them in its concentrated form, particularly when aided by the application of heat. But *nitrous acid* and *nitrogen tetroxide* decompose hydriodic acid and iodides with the greatest facility, even in the most dilute solutions. Colorless solutions of iodides therefore acquire immediately a brownish-red color upon addition of some red fuming nitric acid, or of a mixture of this with concentrated sulphuric acid, or better still, upon addition of nitrosulphonic acid,* or of potassium nitrite and some sulphuric or hydrochloric acid. From more concentrated solutions the iodine separates in the form of black scales, whilst nitrogen oxides and iodine vapor escape.

8. As the blue coloration of IODIZED STARCH (see 1), remains visible in much more highly dilute solutions than the yellow color of solution of iodine in water, the delicacy of the reaction just now described (7) is considerably heightened by mixing the fluid to be tested for iodine first with some thin tolerably clear *starch paste*,† then adding a few drops of dilute sulphuric acid, to make the fluid strongly acid, and finally one of the reagents given in 7. Of nitrosulphonic acid a single drop on a glass rod suffices to produce the reaction most distinctly. Red fuming nitric acid must be added in somewhat larger quantity to call forth the reaction in its highest intensity; this reagent therefore is not well adapted to detect very minute quantities of iodine. The reaction with potassium nitrite also is very delicate. The fluid to be tested is mixed with dilute sulphuric acid or with hydrochloric acid to distinctly acid reaction, and a drop or two of a concentrated solution of potassium nitrite is then added. In cases where the quantity of iodine present is very minute, the fluid turns reddish, instead of blue.

An excess of the fluid containing nitrous acid or nitrogen tetroxide does not materially impair the delicacy of the reaction. As iodized starch becomes colorless in hot water, the fluids must of necessity be cold; the colder they are the more delicate the reaction. To attain the highest degree of delicacy, cool the fluid with ice, let the starch deposit, and place the test-tube upon white paper to observe the reaction (compare also § 157).

9. *Chlorine gas* and *chlorine water* decompose compounds of iodine also, setting the iodine free; but if the chlorine is applied in excess, the liberated iodine combines with it to colorless iodine chloride. A dilute solution of a metallic iodide, mixed with starch paste, acquires therefore upon ad-

* NO_2-SO_2-OH—obtained by heating starch with nitric acid, and passing the evolved gases into oil of vitriol.

† Prepared by heating a mixture of starch with 50 parts of cold water to boiling.

dition of a little chlorine water at once a blue tint, but becomes colorless again upon addition of more chlorine water. As it is therefore difficult not to exceed the proper limit especially where the quantity of iodine present is only small, chlorine water is not well adapted for the detection of minute quantities of iodine.

10. If a solution containing hydriodic acid or an iodide is mixed with *chloroform* or *carbon disulphide*, so as to leave a few drops undissolved, and one of the agents by which iodine is liberated (a drop of a solution of nitrogen tetroxide in sulphuric acid—hydrochloric acid and potassium nitrite—chlorine water, etc.) is added, the mixture vigorously shaken, and then allowed to stand at rest, the chloroform or the carbon disulphide, colored violet-red by the iodine dissolved in it, subsides to the bottom. This reaction also is exceedingly delicate.

11. If metallic iodides are heated with *concentrated sulphuric acid*, or with *sulphuric acid* and *manganese dioxide*, or with *sulphuric acid* and *potassium dichromate*, or with *ferric chloride* and a little *hydrochloric acid*, iodine separates, which may be known by the color of its vapor, or in the case of very minute quantities, by its action upon a slip of paper coated with starch paste.

12. The iodides which are insoluble in water and nitric acid comport themselves upon fusion with *sodium carbonate* in the same manner as the corresponding chlorides.

13. A *sodium metaphosphate bead, saturated with cupric oxide*, when touched with a substance containing iodine, and ignited in the inner blowpipe flame, imparts an intense GREEN color to the flame. With regard to the spectrum of iodide of copper, see § 157.

§ 155.

d. CYANOGEN, C N OR Cy., AND HYDROCYANIC ACID, H C N.

1. CYANOGEN is a colorless gas of a peculiar penetrating odor; it burns with a crimson flame, and is pretty soluble in water.

2. HYDROCYANIC ACID is a colorless, volatile, inflammable liquid, the odor of which distantly resembles that of bitter almonds; it is miscible with water in all proportions; in the pure state it speedily suffers decomposition. It is extremely poisonous.

3. The CYANIDES of the alkali and alkali-earth metals are soluble in water; the solutions smell of hydrocyanic acid

They are readily decomposed by acids, even by carbonic acid. Potassium and sodium cyanides are not decomposed by fusion if air is excluded; when fused with oxides of lead, copper, antimony, tin, etc., they reduce these oxides, and are converted into cyanates. Only a few of the cyanides with heavy metals are soluble in water; all of them are decomposed by ignition, the cyanides of the noble metals being converted into cyanogen gas and metal, the cyanides of the other heavy metals into nitrogen gas and metallic carbides. Many of the cyanides of heavy metals are not decomposed by dilute oxygen acids, and only with difficulty by concentrated nitric acid. By heating and evaporation with concentrated sulphuric acid all cyanides are decomposed; hydrochloric acid decomposes a few of them; hydrosulphuric acid decomposes many cyanides.

4. The CYANIDES have a great tendency to combine with each other; hence most of the cyanides of the heavy metals dissolve in potassium cyanide. The resulting compounds are either:

a. Double salts, *e g.*, nickel potassium cyanide, $Ni(CN)_2 + 2KCN$. From solutions of such double salts, acids, by decomposing the potassium cyanide, precipitate the metallic cyanide which was combined with it.—Or,

b. Haloid salts, in which a metal, *e.g.*, potassium, is combined with a compound radical consisting of cyanogen and another metal (iron, cobalt, manganese, chromium). The ferro- and the ferricyanide of potassium ($Fe(CN)_2.4KCN$, also $K_4 Fe Cy_6$ or $K_4 Cfy$ and $Fe_2(CN)_6.6KCN$, also $K_6 Fe_2 Cy_{12}$, or $K_6 Cfdy$), and cobalticyanide of potassium ($K_6 Co_2 Cy_{12}$)* are compounds of this kind. From solutions of compounds of this nature dilute acids do not separate metallic cyanides in the cold. If the potassium is replaced by hydrogen, corresponding hydrogen acids are formed, which must not be confounded with hydrocyanic acid.

We will now first consider the reactions of hydrocyanic acid and the simple cyanides, then, in an appendix to this paragraph, those of hydroferro- and hydroferricyanic acid.

5. *Silver nitrate* produces in solutions of free hydrocyanic acid and of cyanides of the alkali metals white precipitates of SILVER CYANIDE, Ag Cy, which are readily soluble in potassium cyanide, dissolve with some difficulty in ammonia, and are insoluble in dilute nitric acid; these precipitates are decomposed by ignition, leaving metallic silver with some silver paracyanide.

6. If a solution of *ferrous sulphate* and a few drops of *ferric chloride* are added to a solution of free hydrocyanic acid, no

* In ferrocyanides Fe is bivalent (ferrous); in ferricyanides and cobalticyanides Fe_2 and Co_2 are sexivalent (ferric and cobaltic). See page 261.

alteration takes place; but if *solution of potassa* or *soda* is now added a bluish-green precipitate forms, which consists of a mixture of Prussian-blue, $Fe_7 Cy_{18}$, and ferrous-ferric hydroxide. Upon now adding hydrochloric acid (best after previous application of heat) the ferrous-ferric hydroxide dissolves, whilst the PRUSSIAN-BLUE remains undissolved. If only a very minute quantity of hydrocyanic acid is present the fluid simply appears green after the addition of the hydrochloric acid, and it is only after long standing that a trifling blue precipitate separates from it. The same final reaction is observed when a mixture of ferrous and ferric salt is mixed with the solution of an alkali cyanide, and hydrochloric acid is then added.

7. If a liquid containing a little hydrocyanic acid or potassium cyanide is mixed with sufficient yellow ammonium sulphide to impart a yellowish tint to the fluid, then with a little ammonia, and the mixture is warmed in a porcelain dish, with renewal of the water if necessary, until it has become colorless, and the excess of ammonium sulphide is decomposed or volatilized, the fluid contains now ammonium sulphocyanate, and after being acidified with hydrochloric acid (which must not be attended with disengagement of hydrosulphuric gas), acquires a blood-red tint upon addition of ferric chloride (v. LIEBIG). This reaction is exceedingly delicate. The following formula expresses the transformation of hydrocyanic acid into ammonium sulphocyanate, $N H_4 S_2 + 4 N H_3 + 4 H Cy = 4 (N H_4 Cy S) + N H_4 S$. If an acetate* is present the reaction takes place only upon addition of more hydrochloric acid. To discover the cyanogen *in insoluble compounds* by converting it into ferric sulphocyanate you may proceed as follows: Fuse some sodium thiosulphate ("hyposulphite of soda") in the loop of a platinum wire till the water of crystallization has escaped, and the mass swells out, dip it in the substance, heat for a little time, removing it from the flame as soon as the sulphur begins to burn, and then dip the mass in a few drops of ferric chloride mixed with a little hydrochloric acid. A permanent blood-red color will be produced. If the substance is heated too long the reaction fails, as the sodium sulphocyanate formed is then destroyed again. This method is well suited to distinguish silver chloride, bromide, or iodide from cyanide (A. FRÖHDE).

8. On mixing a moderately concentrated solution of an alkali metal cyanide with a little picric acid solution (1 of picric acid to 250 of water) and boiling, the fluid appears dark-red from formation of alkali metal picrocyanate, the coloration increasing in intensity by standing. If the solution of the cyanide is very dilute, no more picric acid must be added than is sufficient just to color the fluid lemon yellow. After boiling, the red coloration often does not make its appearance till the fluid has cooled and stood some time. The reaction is very delicate (C. D. BRAUN).

9. On saturating filter paper with freshly prepared tincture of guaiacum containing 3 or 4 per cent. of the resin, allowing the alcohol to evaporate,

* Or one of the salts mentioned § 111, 8.

moistening the paper with solution of copper sulphate containing ½ per cent. of the salt, and then exposing it to air, in which a trace of hydrocyanic acid is present, it becomes blue from liberation of oxygen, $8Cu\,O + 4H\,Cy = Cu_2\,Cy_4 + 2H_2\,O + O$ (PAGENSTECHER, SCHÖNBEIN).

10. If a very dilute solution of iodized starch is mixed with a trace of hydrocyanic acid, or after addition of dilute sulphuric acid, with a trace of an alkali-metal cyanide, the blue color will disappear immediately, or after a short time, the iodine and the hydrocyanic acid being transformed into cyanogen iodide and hydriodic acid (SCHÖNBEIN). This is a very delicate reaction, but cannot be relied upon without further tests, as many other substances decolorize iodized starch.

11. Neither of the above methods will serve to effect the detection of cyanogen in mercuric cyanide. To detect cyanogen in that compound the solution is mixed with hydrosulphuric acid; mercuric sulphide precipitates, and the solution contains free hydrocyanic acid. In solid mercuric cyanide the cyanogen is most readily detected by heating in a glass tube. (Compare 8.)

Appendix.

a. Hydroferrocyanic acid, $H_4\,Fe''\,Cy_6$ or $H_4\,Cfy$. Hydroferrocyanic acid is soluble in water. Some of the ferrocyanides, as those containing alkali and alkali-earth metals, are soluble in water; but the greater part of them are insoluble in that menstruum. All the ferrocyanides are decomposed by ignition; where they are not quite anhydrous, hydrocyanic acid, carbonic acid, and ammonia escape, otherwise nitrogen and occasionally cyanogen. In solutions of hydroferrocyanic acid or ferrocyanides *ferric chloride* produces a blue precipitate of FERRIC FERROCYANIDE, $Fe_4'''\,(Fe''\,Cy_6)_3$ or $Fe_7\,Cy_{18}$; *cupric sulphate* a brownish-red precipitate of CUPRIC FERROCYANIDE, $Cu_2\,Fe\,Cy_6$; *silver nitrate* a white precipitate of ARGENTIC FERROCYANIDE, $Ag_4\,Fe\,Cy_6$, which is insoluble in nitric acid and in ammonia, but dissolves in potassium cyanide. If a not too dilute solution of an alkali-metal ferrocyanide is mixed with *hydrochloric acid*, and some *ether* is poured on the top of the mixture, HYDROFERROCYANIC ACID will separate in the crystalline form where the two fluids meet. Insoluble ferrocyanides are decomposed by boiling with solution of soda, sodium ferrocyanide being formed, and the metals separate as hydroxides, unless they are soluble in soda. If ferrocyanides are heated with a mixture of 3 parts concentrated sulphuric acid, and 1 part water, till the free acid is expelled, they are decomposed, and the cyanogen is driven off in the form of hydrocyanic acid; the metals remain behind as sulphates. On

projecting metallic cyanides into fusing potassium nitrate, the cyanogen is converted into carbon dioxide and nitrogen, and the metals are converted into oxides, which remain in the crucible.

b. Hydroferricyanic acid, $H_6 Fe_2''' Cy_{12}$, or H_6Cfdy. Hydroferricyanic acid and many of the ferricyanides are soluble in water; all ferricyanides are decomposed by ignition like the ferrocyanides. In the aqueous solutions of hydroferricyanic acid and its salts *ferric chloride* produces no blue precipitate; but *ferrous sulphate* produces a blue precipitate of FERROUS FERRICYANIDE, $Fe_3'' Fe_2''' Cy_{12}$ or $Fe_3 Cfdy$; cupric *sulphate* a yellowish green precipitate of CUPRIC FERRICYANIDE, $Cu_3 Cfdy$, which is insoluble in hydrochloric acid; *silver nitrate* an orange-colored precipitate of SILVER FERRICYANIDE, $Ag_6 Cfdy$, which is insoluble in nitric acid, but dissolves readily in ammonia and in potassium cyanide. The insoluble ferricyanides are decomposed by boiling in solution of soda, metallic oxides, or hydroxides being thrown down; in the fluid filtered off from them either sodium ferricyanide alone is found, or a mixture of sodium ferro- with ferricyanide. By heating with a mixture of 3 parts concentrated sulphuric acid, and 1 part water, and also by fusing with potassium nitrate, the ferricyanides are decomposed like the ferrocyanides.

§ 156.

e. SULPHUR, S. 32, and HYDROSULPHURIC ACID, $H_2 S$.

1. SULPHUR is a solid, brittle, friable, tasteless body, insoluble in water. It occurs occasionally in the form of yellow or brownish crystals, or crystalline masses of a yellow or brownish color, and occasionally in that of a yellow or yellowish-white, or grayish white powder. It melts at a moderate heat; upon the application of a stronger heat it is converted into brownish-yellow vapors, which in cold air condense to a yellow powder, and on the sides of the vessel to drops. Heated in the air it burns with bluish flame to sulphur dioxide, which betrays its presence at once by its suffocating odor. Concentrated nitric acid, nitrohydrochloric acid, and a mixture of potassium chlorate and hydrochloric acid, or, better, nitric acid, dissolve sulphur gradually, with the aid of a moderate heat, and convert it into sulphuric acid; in boiling solution of soda, sulphur dissolves to a yellow fluid, which contains sodium polysulphide and sodium thiosulphate, $Na_2 S_2 O_3$; in cold ammonia it is insoluble, in warm ammonia it dissolves to a small extent. Carbon disulphide dissolves the ordinary variety of sulphur with ease, but there is a kind which is insoluble in this menstruum.

2. HYDROSULPHURIC ACID, HYDROGEN SULPHIDE OR SULPHURETTED HYDROGEN,

at the common temperature, and under common atmospheric pressure, is a colorless inflammable gas, soluble in water, readily recognized by its smell of rotten eggs; it transiently imparts a red tint to moist litmus paper.

3. Of the SULPHIDES only those of alkali and alkali-earth metals are soluble in water. These, as well as the sulphides of iron, manganese, and zinc, are decomposed by dilute mineral acids, with evolution of hydrosulphuric acid gas, which may be readily detected by its smell, and by its action upon solution of lead (see 4). The decomposition of polysulphides is attended also with separation of sulphur in a finely divided state; the white precipitate may be readily distinguished from similar precipitates by its deportment on heating. Part of the sulphides of the metals of the fifth and sixth groups are decomposed by concentrated and boiling hydrochloric acid, with evolution of hydrosulphuric acid gas, whilst others are not dissolved by hydrochloric acid, but by concentrated and boiling nitric acid. The compounds of sulphur with mercury, gold, and platinum, resist the action of both acids, but dissolve in nitrohydrochloric acid. Upon the solution of sulphides in nitric acid, and in nitrohydrochloric acid, sulphuric acid is formed, and in most cases sulphur is also separated. Many metallic sulphides, more especially those of a higher degree of sulphuration, give a sublimate of sulphur when heated in a tube sealed at one end. All sulphides are decomposed by fusion with sodium nitrate and carbonate; on extracting the fusion with water the sulphur is found in solution as sodium sulphate.

4. If hydrosulphuric acid, in the gaseous state or in solution, is brought into contact with *silver nitrate* or *lead acetate*, black precipitates of SILVER SULPHIDE or LEAD SULPHIDE are formed. In cases therefore where the odor fails to afford sufficient proof of the presence of hydrosulphuric acid, these reagents will remove all doubt. If the hydrosulphuric acid is present in the gaseous form the air suspected to contain it is tested by placing in it a small slip of paper moistened with solution of lead acetate and a little ammonia; if the gas is present the slip becomes covered with a brownish-black shining film of lead sulphide. To detect a trace of an alkali sulphide in presence of a free alkali or an alkali carbonate, the best way is to mix the fluid with a solution of lead hydroxide in soda, which is prepared by mixing solution of lead

acetate with solution of soda until the precipitate which forms at first is redissolved.

5. If a fluid containing hydrosulphuric acid or an alkali sulphide is mixed with solution of soda, then with *sodium nitroprusside*,* it acquires a fine reddish-violet tint. The reaction is very delicate; but that with solution of lead hydroxide in soda is still more sensitive.

6. If metallic sulphides are exposed to the *oxidizing flame of the blowpipe*, the sulphur burns with a blue flame, emitting at the same time the well-known odor of sulphur dioxide. If a metallic sulphide is heated in a glass tube open at both ends, in the upper part of which a slip of blue litmus paper is inserted, and the tube is held in a slanting position during the operation, the escaping sulphur dioxide reddens the litmus paper.

7. If a finely pulverized metallic sulphide is boiled in a porcelain dish with solution of soda, and the mixture heated to incipient fusion of the caustic soda, or if the test specimen is fused in a platinum spoon with caustic soda, and the mass is, in either case, dissolved in a little water, a piece of bright silver (a polished coin) put into the solution, and the fluid warmed, a brownish black film of silver sulphide forms on the metal. This film may be removed afterwards by rubbing the metal with leather and quicklime (v. KOBELL).

8. If the powder of a sulphide which is decomposed by hydrochloric acid with difficulty, or not at all, is mixed in a small cylinder, or in a wide-necked flask, with an equal volume of finely divided iron free from sulphur (ferrum alcoholisatum), and some moderately dilute hydrochloric acid (1 volume of concentrated acid to 1 volume of water) is poured over the mixture, in a layer a few lines thick, hydrosulphuric acid escapes along with the hydrogen. This may be easily detected by placing a slip of paper moistened with solution of lead acetate, and dried again, under the cork, so that the bottom is covered by it, the ends of the slip projecting on both sides, and then loosely inserting the cork into the mouth of the flask. Realgar, orpiment, and molybdenite do not show this reaction (v. KOBELL).

§ 157.

Recapitulation and remarks.—Most of the acids of the first group are also precipitated by silver nitrate, but the precipitates cannot well be confounded with the silver compounds of the acids of the second group, since the former are soluble in dilute nitric acid, whilst the latter are insoluble in that menstruum. The presence of HYDROSULPHURIC ACID interferes

* As nitroprusside of sodium can very well be dispensed with, I have omitted giving it a place among the reagents.

with the testing for the other acids of the second group; this acid must therefore, if present, be removed before the testing for the other acids can be proceeded with. The removal of the hydrosulphuric acid, when present in the free state, may be effected by simple ebullition; and when present in the form of an alkali sulphide, by the addition of a metallic salt, such as will not precipitate any of the other acids, or at least will not precipitate them from acid solutions. HYDRIODIC and HYDROCYANIC ACIDS may be detected, even in presence of hydrochloric or hydrobromic acid, by the equally characteristic and delicate reactions with starch or carbon disulphide (with addition of a fluid containing nitrous acid), and with solution of ferrous with a little ferric salt.

The detection of CHLORINE and BROMINE is more or less difficult in presence of iodine and cyanogen. These latter must therefore, if present, be removed before the tests for chlorine or bromine can be applied. The separation of the cyanogen may be readily effected by converting the whole of the radicals present into silver salts and igniting; the silver cyanide is decomposed in this process, whilst the chloride, bromide, and iodide of silver remain unaltered. Upon fusing the ignited residue with sodium carbonate and boiling the fused mass with water, sodium chloride, bromide, and iodide are obtained in solution. The fused silver compounds may also be readily decomposed with zinc; all that is required for this purpose is to pour water over them, to add a little sulphuric acid and a fragment of zinc, to let the mixture stand some time, and finally to filter the solution of zinc chloride, bromide, or iodide from the separated metallic silver.

The iodine may be separated from the chlorine and bromine, by treating the silver compounds with ammonia, but more accurately by precipitating the iodine as cuprous iodide. From bromine, iodine is separated most accurately by palladious chloride, which only precipitates the iodine; from chlorine it is separated by palladious nitrate.

BROMINE in presence of iodine and chlorine may be identified by the following simple operation: Mix the fluid with a few drops of dilute sulphuric acid, then with some starch paste, and add a little red fuming nitric acid or, better still, a solution of nitrosulphonic acid, whereupon the iodine reaction will show itself immediately. Add now chlorine water drop by drop until that reaction has disappeared; then add

some more chlorine water to set the bromine also free, which may then be separated and identified by means of chloroform or carbon disulphide.

Or, the iodine after being liberated in a highly dilute fluid may be also taken up with chloroform or carbon disulphide, the aqueous fluid may then be filtered through a moist filter, and the bromine detected in the filtrate by means of chloroform or carbon disulphide and chlorine water. For the latter process you may substitute the following: Immediately after the liberation of the iodine, cautiously add chlorine water, when the violet-red coloration will gradually fade away, and give place to the brownish-red color indicative of bromine.

The detection of CHLORIDES in presence of bromides and iodides is best effected by precipitating with silver nitrate, washing the precipitate, digesting it with a mixture of 1 part ammonia and 3 parts water, filtering off the silver iodide, precipitating the filtrate with nitric acid, washing the precipitate (which contains silver chloride and bromide with a trace of iodide), drying it, fusing with sodium carbonate, extracting the fusion with water, neutralizing the solution with sulphuric acid (the reaction may be somewhat alkaline), evaporating to dryness, and treating the residue according to § 152, 7. The presence of much iodine interferes with the reaction, therefore it is directed to be removed.

[Or, the moist silver chloride, etc., may be treated with metallic zinc and a little dilute sulphuric acid, for some time. The resulting solution of Zn Cl (with a little Zn Br and a trace of Zn I) is freed from zinc by heating to boiling, adding a slight excess of Na_2CO_3 solution and filtering. The filtrate containing the sodium salts is evaporated to dryness, mixed with potassium dichromate and distilled with sulphuric acid (§ 152, 7)].

As regards the starch reaction, it must be noted that many salts (alum, alkali sulphates, magnesium sulphate, etc.), diminish its delicacy. Also as regards this and the carbon disulphide reaction, when nitrogen tetroxide is used to liberate the iodine, the presence of sulphocyanates may occasion mistakes (NADLER,) since a reddish color may occur in the absence of iodine, from formation of pseudosulphocyanogen. By shaking with carbon disulphide the coloring substance is for the most part taken up.

Besides the above mentioned agents for liberating iodine many others have been proposed, and may be employed; thus, for instance, iodic acid or alkali iodate and hydrochloric acid (v. LIEBIG); ferric chloride and sulphuric acid, or platinic chloride with addition of some hydrochloric acid (HEMPEL); potassium permanganate in slightly acidified solution (HENRY), etc. With respect to these agents I have to observe that iodic acid must be used with the greatest

caution, as *a*, in presence of reducing substances iodine is set free from the reagent, and *b*, an excess of iodic acid will at once put an end to the reaction. Ferric chloride, with addition of sulphuric acid, will not act immediately upon very dilute solutions, but after a time the reaction will make its appearance, revealing the presence of even the minutest trace of iodine; the delicacy of the reaction is not materially impaired by an excess of the reagent. Ferric chloride may be used with advantage when iodine is to be liberated in the gaseous state, which should be done in the presence of sulphocyanates. The fluid is then heated nearly to boiling, and the escaping fumes are made to act on paper smeared with fresh starch paste. Potassium permanganate acts immediately, even in the most dilute solutions. However, as a fluid colored by minute traces of iodized starch is also apt to look reddish, the coloration imparted by the permanganic acid alone may lead to mistakes in using the starch test. From six to twelve hours should therefore always be allowed to elapse before judging of the actual nature of the coloration. The *modus operandi* may of course be modified in various ways to increase the delicacy of the starch reaction; interesting particulars upon this point may be found in the papers of MORIN* and HEMPEL.†

Chlorine, bromine, and iodine may also be distinguished from each other by the spectroscope, for the spectra of their copper salts, though containing many blue and green lines, vary in the position and prominence of the lines; they may also be detected in presence of one another, for by cautiously heating the silver salts with cupric oxide in a current of hydrogen, and lighting the escaping gas, the flame will be colored first by the copper chloride, then by the copper bromide, and lastly by the copper iodide (AL. MITSCHERLICH).‡ The use of this method requires considerable practice, in consequence of the similarity of the spectra, and the method therefore appears to me of more scientific interest than practical importance.

§ 158.

Rarer Acids of the Second Group.

1. NITROUS ACID, HNO_2, OR NO.OH.

NITROSYL, NO, is a colorless gas evolved in the action of the metals (copper, silver, etc.), on nitric acid; mixed with ½ its volume of oxygen it forms at low temperatures N_2O_3; with ½ its volume of oxygen it yields at common temperatures a mixture of nitryl, NO_2, and nitrogen tetroxide or dinitryl, N_2O_4. NITROGEN TRIOXIDE or NITROUS ANHYDRIDE, N_2O_3, exists as a deep blue liquid at temperatures below 0°. Above 0° it decomposes partially into NO, NO_2 and N_2O_4, and at common temperatures the mixture appears as a brownish-red gas. In contact with a little cold water it yields probably nitrous acid, $N_2O_3 + H_2O = 2(HNO_2)$. With much and warm water it is converted for the most part into nitric acid, which dissolves, and nitrosyl, which escapes as gas when the quantity of water is not very large, $3N_2O_3 + H_2O = 2HNO_3 + 4NO$.

* Journ. f. prakt. Chem., 78, 1. † Ann. d. Chem. u. Pharm., 107, 102.
‡ Zeitschr. f. anal. Chem., 4, 153.

NITROGEN TETROXIDE, N_2O_4, at 20° is a colorless crystalline mass which melts at 12° and boils at 28°, yielding a red gas, a mixture of N_2O_4 and NO_2. Mixed with water it yields nitrous and nitric acid, $N_2O_4 + H_2O = HNO_2 + HNO_3$. With an alkali it yields a nitrite and a nitrate.

The NITRITES are decomposed by ignition; many of them are soluble in water. When nitrites or concentrated solutions of nitrites are treated with dilute sulphuric acid, nitric acid is formed and nitrosyl is evolved. In concentrated solutions of alkali nitrites, *silver nitrate* produces a white precipitate, which dissolves in a very large proportion of water, especially upon application of heat; *ferrous sulphate*, upon addition of a small quantity of acid, produces a dark blackish-brown coloration, which is due to the nitrosyl dissolving in the ferrous solution. *Hydrosulphuric acid* produces in solutions containing nitrous acid, after neutralization by an acid of the free alkali, should any be present, a copious precipitate of sulphur, the reaction being attended also with formation of ammonium nitrate. *Pyrogallic acid* imparts a brown color to even very dilute solutions of nitrites acidified with sulphuric acid (SCHÖNBEIN). On addition of *potassium cyanide* to an alkaline nitrite, then of some neutral solution of *cobalt chloride*, and a little acetic acid, the fluid becomes orange-rose colored from the formation of cobalt potassium nitrocyanide (C. D. BRAUN). But the most delicate reagent for nitrous acid is solution of *potassium iodide mixed with starch paste*, especially upon addition of sulphuric acid (PRICE, SCHÖNBEIN). Water containing the one hundred thousandth part of potassium nitrite, together with free sulphuric acid, is colored distinctly blue by this reagent in a few seconds, and a few minutes suffice to produce the same effect in water containing one millionth part of potassium nitrite. This reaction is trustworthy only where no other substance is present that might exercise a decomposing action upon potassium iodide, such, for instance, as iodic acid, ferric salts, etc. On adding *indigo solution* to water till the latter has lost its transparence from the depth of color, then hydrochloric acid and afterwards a solution of *alkali polysulphide* with stirring, till the blue color just vanishes, filtering and adding to the clear filtrate a solution of the merest trace of nitrous acid, a most distinct bluish coloration will at once be produced. This reaction is to be recommended in the presence of other reducing bodies which interfere with the action of nitrous acid upon an acidified solution of starch and potassium iodide (SCHÖNBEIN). But it must not be overlooked that other oxidizing substances reproduce the blue color. On mixing a solution of nitrous acid (for instance, a solution of potassium nitrite acidified with acetic acid) with *potassium sulphocyanate* the fluid is not colored, but on the further addition of nitric acid, a dark-red color makes its appearance, which vanishes on addition of alcohol or after heating for a short time (difference from ferric sulphocyanate). The coloring substance is mostly taken up from this by shaking with carbon disulphide. It will be evident that this reaction is due to nitryl, and not to nitrous acid, hence it may be used to distinguish between the two.

2. HYPOCHLOROUS ACID, HClO.

HYPOCHLOROUS OXIDE, Cl_2O, at the common temperature, is a deep yellowish-green gas of a disagreeable irritating odor, similar to that of chlorine. It dissolves in water, forming HYPOCHLOROUS ACID, $Cl_2O + H_2O = 2HClO$;

the dilute aqueous solution bears distillation. The HYPOCHLORITES are usually found in combination with metallic chlorides, as is the case, for instance, in "chloride of lime" or calcium hypochlorite, *plus* calcium chloride, $Ca\,Cl_2\,O_2 + Ca\,Cl_2$, *eau de Javelle*, or solution of sodium hypochlorite, *plus* sodium chloride. The solutions of hypochlorites undergo alteration by boiling, the hypochlorite being resolved into chloride and chlorate, attended in the case of concentrated, but not in that of dilute solutions, with evolution of oxygen. If a solution of "chloride of lime" is mixed with hydrochloric acid or sulphuric acid, chlorine is disengaged, whilst addition of a little nitric acid leads to the liberation of hypochlorous acid. *Silver nitrate* throws down from solution of "chloride of lime" silver chloride [the silver hypochlorite which forms at first is speedily resolved into silver chloride and chlorate, $3Ag\,Cl\,O = Ag\,Cl\,O_3 + 2Ag\,Cl$]; *lead nitrate* produces a precipitate which from its original white changes gradually to orange-red, and ultimately, owing to formation of lead dioxide, to brown; *manganese salts* give brown-black precipitates of manganese dioxide. Solution of potassium permanganate is not decolorized. Solutions of *litmus* and *indigo* are decolorized even by the alkaline solutions of hypochlorites, but still more rapidly and completely upon addition of an acid. If a solution of arsenious oxide in hydrochloric acid is colored blue with solution of indigo, and a solution of "chloride of lime" is added, with active stirring, the decoloration will take place only after the whole of the arsenious oxide has been converted to arsenic acid.

3. CHLOROUS ACID, $H\,Cl\,O_2$.

CHLOROUS OXIDE, $Cl_2\,O_3$, is a yellowish-green gas of a peculiar and very disagreeable odor; it is soluble in water, with production of CHLOROUS ACID. The solution has an intensely yellow color, even when highly dilute. Most of the CHLORITES are soluble in water; the solutions readily suffer decomposition, the chlorites being resolved into chlorides and chlorates. *Silver nitrate* precipitates white silver chlorite, which is soluble in much water. A solution of *potassium permanganate* is immediately decomposed, and a brown precipitate separates after some time. *Tincture of litmus* and *solution of indigo* are instantly decolorized, even if mixed with arsenious oxide in excess. If a slightly acidified dilute solution of a *ferrous salt* is mixed with a dilute solution of chlorous acid, the fluid transiently acquires an amethyst tint, and assumes only after the lapse of a few seconds the yellowish coloration of ferric salts (LENSSEN).

4. HYPOPHOSPHOROUS ACID, $H_3\,P\,O_2$.

The concentrated solution of HYPOPHOSPHOROUS ACID is of a syrupy consistence, and resembles that of phosphorous acid (see § 148), with which it also has this in common, that it is resolved by heating, with exclusion of air, into phosphoric acid and not spontaneously inflammable phosphoretted hydrogen gas. Almost all hypophosphites are soluble in water; by ignition all of them are resolved into phosphate and phosphoretted hydrogen, which in most cases is spontaneously inflammable. *Barium chloride*, *calcium chloride*, and *lead acetate* fail to precipitate solutions of hypophosphites (difference from phosphorous acid). *Silver nitrate* gives with hypophosphites at first a white precipitate of silver hypophosphite, which turns black even at the common tem-

perature, but more rapidly on heating, the change of color being attended with separation of metallic silver. From excess of *mercuric chloride*, hypophosphorous acid precipitates mercurous chloride slowly in the cold, more rapidly on heating. With *zinc* and *dilute sulphuric acid* hypophosphorous acid gives hydrogen mixed with phosphoretted hydrogen. (Compare § 148, Phosphorous Acid.)

Third Group.

Acids which are not precipitated by Barium Salts nor by Silver Salts: *Nitric Acid, Chloric Acid* (Perchloric Acid).

§ 159.

a. Nitric Acid, $H N O_3$, or $NO_2 . OH$.

1. Nitrogen pentoxide, $N_2 O_5$, crystallizes in six-sided prisms. It fuses at 29.5° and boils at about 45° (Deville). Pure nitric acid is a colorless, exceedingly corrosive fluid, which emits fumes in the air, exercises a rapidly destructive action upon organic substances, and colors the albuminoids intensely yellow. Nitric acid containing nitrogen tetroxide, $N_2 O_4$, or nitryl, NO_2,* has a red color.

2. All the normal salts of nitric acid are soluble in water; only some of the basic nitrates are insoluble. All nitrates undergo decomposition at an intense red heat. Nitrates of the alkali metals at first yield oxygen, and change to nitrites, afterwards they yield oxygen and nitrogen. Those with other bases yield oxygen and nitrogen trioxide, $N_2 O_3$, or nitryl, NO_2.

3. If a nitrate is thrown upon *red-hot charcoal*, or if charcoal or some organic substance, paper for instance, is brought into contact with a nitrate in fusion, deflagration takes place, *i. e.*, the charcoal burns at the expense of the oxygen of the nitric acid, with vivid scintillation.

4. If a mixture of a nitrate with *potassium cyanide* in powder is heated (*use very small quantities!*) on platinum foil, a vivid deflagration ensues, attended with distinct ignition and detonation. Even very minute quantities of nitrates may be detected by this reaction.

* As great confusion exists in the nomenclature of the oxides of nitrogen, the following statement of the symbols and names employed in this edition is given.

$N_2 O_5$	= Nitrogen	pentoxide	or nitric anhydride.
$N_2 O_4$	= "	tetroxide	" dinitryl.
$N_2 O_3$	= "	trioxide	" nitrous anhydride.
$N_2 O$	= "	monoxide	" hyponitrous anhydride.
NO_2	=		nitryl.
NO	=		nitrosyl.

5. If a nitrate is mixed with *copper filings*, and the mixture heated in a test-tube with concentrated sulphuric acid, the air in the tube acquires a yellowish-red tint, owing to the nitrosyl, NO, which is liberated upon the oxidation of the copper by the nitric acid, combining with the oxygen of the air to form nitryl and dinitryl. The coloration may be observed most distinctly by looking lengthways through the tube.

6. If the solution of a nitrate is mixed with an equal volume of concentrated *sulphuric acid*, free from nitric acid and oxides of nitrogen, the mixture allowed to cool, and a concentrated solution of *ferrous sulphate* then cautiously added to it so that the fluids do not mix, the junction shows at first a purple, afterwards a brown color, or, in cases where only a very minute quantity of nitric acid is present, a reddish color. On mixing the fluids a brownish purple-red *clear* fluid is obtained. In this process nitrosyl is formed,* which unites with a portion of ferrous salt, and forms with it a peculiar compound, which dissolves in water to a brownish-black color. A similar reaction is observed in presence of selenious acid; but on mixing the fluid, and letting it stand, red selenium separates (WITTSTOCK).

7. If a little *brucia* is dissolved in pure concentrated sulphuric acid (to which it gives a faint rose tint) and a small quantity of a fluid containing nitric acid added to the solution, the latter immediately acquires a magnificent red color. This reaction is extraordinarily delicate. The color soon passes into reddish yellow. Chloric acid gives the same reaction.

8. Dissolve one part of *carbolic acid* in four parts of strong sulphuric acid, and add two parts of water. A drop or two of this fluid added to a solid nitrate (*e. g.*, to the residue obtained by evaporating a few drops of well-water containing nitrates) gives a reddish-brown color, from the formation of a nitro-compound. On addition of a drop or two of strong ammonia, this color turns yellow, sometimes passing through a green shade. A very delicate reaction (H. SPRENGEL).

9. If some hydrochloric acid is boiled in a test-tube, one or two drops of very dilute *indigo solution* added, and the mixture boiled again, the fluid remains

* $6\,FeSO_4 + 3\,H_2SO_4 + 2\,HNO_3 = 2\,NO + 4H_2O + 3\,Fe_2(SO_4)_3$.

blue (provided the hydrochloric acid was free from chlorine). If a nitrate, solid or in solution, is now added to the faint light-blue fluid, and the mixture heated again to boiling, the color disappears owing to the decomposition of the indigo blue. This is a most delicate reaction. It must be borne in mind, however, that several other substances also cause decoloration of solution of indigo—free chlorine more particularly produces this effect.

10. Very minute quantities of nitric acid may be detected also by reducing the nitric acid first to nitrous acid, which may be effected both in the moist and in the dry way; in the former by heating the solution of the nitric acid or of the nitrate for some time with finely divided zinc, best with zinc amalgam, and then filtering (SCHÖNBEIN); in the dry way by fusing the substance with sodium carbonate at a moderate heat, extracting the mass, after cooling, with water, and filtering. Upon adding either of the filtrates to a solution of potassium iodide mixed with starch paste and dilute sulphuric acid the fluid acquires a blue color from iodized starch (comp. § 158, 1).

§ 160.

b. CHLORIC ACID, $HClO_3$.

1. CHLORIC ACID, in its most highly concentrated solution, is a colorless or slightly yellowish oily fluid; its odor resembles that of nitric acid. It first reddens litmus, then bleaches it. Dilute chloric acid is colorless and inodorous.

2. All CHLORATES are soluble in water. When chlorates are heated to redness, the whole of the oxygen escapes and metallic chlorides remain.

3. Heated with *charcoal* or some organic substance the chlorates DEFLAGRATE, and this with far greater violence than the nitrates.

4. If a mixture of a chlorate with *potassium cyanide* is heated on platinum foil, DEFLAGRATION takes place attended with strong detonation and ignition, even though the chlorate be present only in minute quantity. This experiment should be made with very small quantities *and with great caution!*

5. If the solution of a chlorate is colored light blue with *solution of indigo*, a little dilute sulphuric acid added, and a solution of sodium sulphite dropped cautiously into the blue fluid, the color of the indigo disappears immediately, The cause of this equally characteristic and delicate reaction is, that the sulphurous acid deprives the chloric acid of its oxygen, thus setting free chlorine or a lower oxide of it, which then decolorizes the indigo.

6. If chlorates are heated with moderately dilute *hydrochloric acid* the constituents of the two acids transpose, forming water, chlorine, and chlorine tetroxide: $2\,HClO_3 + 2\,HCl = 2\,H_2O + 2\,Cl + Cl_2O_4$. The test-tube in which the experi-

ment is made becomes filled in this process with a greenish-yellow gas of a very disagreeable odor resembling that of chlorine; the hydrochloric acid acquires a greenish-yellow color. If the hydrochloric acid is colored blue with indigo solution, the presence of very minute quantities of chlorates will suffice to destroy the indigo color at once.

7. If a little chlorate is added to a few drops of *concentrated sulphuric acid* in a watch-glass, the liberated chloric acid breaks up into perchloric acid and chlorine tetroxide: $3\,HClO_3 = HClO_4 + Cl_2O_4 + H_2O$. Chlorine tetroxide imparts an intensely yellow tint to the sulphuric acid, and betrays its presence also by its odor and the greenish color of the evolved gas. The application of heat must be avoided in this experiment, and the quantities operated upon should be very small, since otherwise the decomposition might take place with such violence as to cause a dangerous explosion.

8. Chloric acid shows the same deportment as nitric acid towards *brucia* dissolved in concentrated *sulphuric acid* (LUCK). Compare § 159, 7.

§ 161.

Recapitulation and remarks.—Of the reactions which have been given to effect the detection of NITRIC ACID, those with ferrous sulphate and sulphuric acid, with copper filings and sulphuric acid, with carbolic acid, and also those based upon the reduction to nitrites, give the most positive results; with regard to deflagration with charcoal, detonation with potassium cyanide, decoloration of solution of indigo and coloration with brucia, we have seen that these reactions belong equally to chlorates as to nitrates, and are consequently decisive only where no chloric acid is present. The presence of *free nitric acid* in a fluid may be detected by evaporating in a porcelain dish on the water-bath to dryness, having first thrown in a few white quill-cuttings; yellow coloration of these indicates the presence of nitric acid (RUNGE). The best way to ascertain whether CHLORIC ACID is present or not (in the absence of other oxygen compounds of chlorine) is to ignite the substance, with addition of sodium carbonate, dissolve the mass, and test the solution with silver nitrate. If a chlorate is present, this is converted into a chloride upon ignition, and silver nitrate will produce a precipitate of silver chloride.

However, the process is thus simple only if no chloride is present with the chlorate. In presence of a chloride, the chlorine of the latter must be removed by adding silver nitrate to the solution as long as a precipitate continues to form, and filtering; the filtrate is then, after addition of pure sodium carbonate, evaporated and ignited. It is, however, generally unnecessary to pursue this circuitous way, since the reactions with concentrated sulphuric acid, and with indigo and sulphurous acid, are sufficiently marked and characteristic to afford positive proof of the presence of chloric acid, even in presence of nitrates. The best way of detecting nitric acid in presence of a large proportion of chloric acid is to mix the substance with sodium carbonate in excess, evaporate, ignite the residue gently, but sufficiently long to convert the chlorate into chloride, and then test the residue for nitric acid, or for nitrous acid.

§ 162.

Perchloric Acid, $HClO_4$.

Pure anhydrous perchloric acid is a colorless, mobile fluid, which forms dense white fumes in the air, and explodes with great violence when dropped on wood-charcoal (Roscoe). The hydrate, $HClO_4.H_2O$, crystallizes in needles; the concentrated aqueous solution is oily and heavy. The dilute solution gives by distillation, first water, then dilute acid, and finally concentrated acid. All perchlorates are soluble in water, most of them freely. They are all decomposed by ignition, those with alkali bases leaving chlorides behind, with disengagement of oxygen. *Potassium salts* produce in not too dilute solutions a white crystalline precipitate of potassium perchlorate, $KClO_4$, which is sparingly soluble in water, insoluble in alcohol. *Barium salts* and *silver salts* are not precipitated. Concentrated sulphuric acid fails to decompose perchloric acid in the cold, and decomposes it with difficulty on heating (difference from chloric acid). Hydrochloric acid, nitric acid, and sulphurous acid fail to decompose aqueous solutions of perchloric acid or perchlorates; solution of indigo, therefore, previously added to it, is not decolorized (difference from all other acids of chlorine).

II. Organic Acids.

First Group.

THE ACIDS OF THE FIRST GROUP ARE DECOMPOSED ENTIRELY OR PARTIALLY BY IGNITION.* THE ACIDS ARE DECOMPOSED BY BOILING WITH CONCENTRATED NITRIC ACID.† THEIR CALCIUM SALTS ARE INSOLUBLE OR DIFFICULTLY SOLUBLE IN WATER. THE SOLUTIONS OF THEIR NORMAL ALKALI SALTS ARE NOT PRECIPITATED BY FERRIC CHLORIDE; *Oxalic Acid, Tartaric Acid* (Racemic Acid), *Citric Acid, Malic Acid.*

§ 163.

a. Oxalic Acid.

For the reactions of oxalic acid I refer to § 145.

b. Dextro Tartaric Acid, $C_2H_2(OH)_2(COOH)_2 = C_4H_6O_6$.

1. Ordinary or DEXTRO TARTARIC ACID forms colorless crystals of an agreeable acid taste, which are persistent in the air, and soluble in water and in alcohol. Heated to 100°, tartaric acid loses no water; heated to 170°, it fuses; at a higher temperature it becomes carbonized, emitting during the process a very peculiar and highly characteristic odor, which resembles that of burnt sugar. Aqueous solution of tartaric acid, as also of almost all tartrates, turns the plane of polarization of light towards the right. By heating with nitric acid tartaric acid is converted into oxalic, acetic, and saccharic acids.

2. The TARTRATES of the alkali metals are soluble in water, and so are the tartrates of the metals of the third and fourth groups. Evaporated on the water-bath to syrupy consistence, the solution of ferric tartrate deposits a pulverulent basic salt. Those of the tartrates which are insoluble in water dissolve in hydrochloric or nitric acid. The tartrates suffer decomposition when heated to redness; charcoal separates, and the same peculiar odor is emitted as attends the carbonization of free tartaric acid.

3. If to a solution of tartaric acid, or to that of an alkali

* Oxalic acid, when cautiously heated, partially sublimes unaltered.

† The decomposition of oxalic acid by boiling nitric acid into carbon dioxide and water is but slow.

tartrate, solution of *an aluminic or of a ferric salt* is added in not too large proportion, and then ammonia or potassa, no precipitation of aluminic or ferric hydroxide will ensue, since the double tartrates formed are not decomposed by alkalies. Tartaric acid prevents also the precipitation of several other hydroxides by alkalies.

4. Free tartaric acid produces, with *potassium salts*, and more particularly with the acetate, a sparingly soluble precipitate of HYDROGEN POTASSIUM TARTRATE $C_4 H_5 K O_6$. A similar precipitate is formed when potassium acetate and free acetic acid are added to the solution of the normal tartrate. The hydrogen potassium tartrate dissolves readily in alkalies and mineral acids; tartaric acid and acetic acid do not increase its solubility in water. The separation of the hydrogen potassium tartrate precipitate is greatly promoted by shaking, or by rubbing the sides of the vessel with a glass rod. The delicacy of the reaction may be heightened by concentrating the solution of the tartaric acid. Addition of an equal volume of alcohol heightens the delicacy of the reaction. In the presence of boric acid, potassium fluoride must be used instead of potassium acetate; this forms potassium borofluoride, and prevents the production of the soluble compound of boric acid, tartaric acid, and potassium (BARFOED).

5. *Calcium chloride* added in excess* throws down from solutions of normal tartrates a white precipitate of CALCIUM TARTRATE $C_4 H_4 Ca O_6 + 4$ aq. Presence of ammonium salts retards the formation of this precipitate for a more or less considerable space of time. Agitation of the fluid or friction on the sides of the vessel promotes the separation of the precipitate. The precipitate is crystalline, or invariably becomes so after some time; it dissolves in a cold, not over dilute solution of potassa or soda, pretty free from carbonate, to a clear fluid. But upon boiling the solution, the dissolved calcium tartrate separates again in the form of a gelatinous precipitate, which redissolves upon cooling.

6. *Lime water* added in excess* produces in solutions of normal tartrates—and also in a solution of free tartaric acid,

* Potassium or sodium tartrate dissolves calcium tartrate (as well as certain other salts insoluble in water, such as calcium phosphate, barium sulphate, etc.). Hence the alkali tartrate must be fully decomposed by the reagent.

if added to alkaline reaction—white precipitates which, flocculent at first, assume afterwards a crystalline form; so long as they remain flocculent they are readily dissolved by tartaric acid as well as by solution of ammonium chloride. From these solutions the calcium tartrate separates again, after the lapse of several hours, in the form of small crystals deposited upon the sides of the vessel.

7. *Solution of calcium sulphate* added in excess* fails to produce a precipitate in a solution of tartaric acid; in solutions of normal tartrates of the alkali metals, it produces a trifling precipitate after the lapse of some time.

8. If solution of ammonia is poured upon even a very minute quantity of calcium tartrate, a small fragment of crystallized *silver nitrate* added, and the mixture slowly and gradually heated, the sides of the test-tube are covered with a bright coating of metallic silver. If, instead of a crystal, solution of silver nitrate be used, or heat be applied more rapidly, the reduced silver will separate in a pulverulent form (ARTHUR CASSELMANN).

9. *Lead acetate* produces white precipitates in solutions of tartaric acid and its salts. The washed precipitate ($C_4 H_4 Pb O_6$) dissolves readily in nitric acid and in ammonia free from carbonic acid.

10. *Silver nitrate* does not precipitate free tartaric acid; but in solutions of normal tartrates it produces a white precipitate of SILVER TARTRATE ($C_4H_4 Ag_2 O_6$), which dissolves readily in nitric acid and in ammonia; upon boiling it turns black, owing to reduction of the silver.

11. Upon heating tartaric acid or a tartrate with *concentrated sulphuric acid*, the latter acquires a brown color almost simultaneously with the evolution of gas.

§ 164.

c. CITRIC ACID, $C_3 H_4 (O H)(C O O H)_3 = C_6 H_8 O_7$.

1. CRYSTALLIZED CITRIC ACID, obtained by the cooling of its solution, has the formula $2 C_6 H_8 O_7 . H_2 O$. It crystallizes in pellucid, colorless and inodorous crystals of an agreeable strongly acid taste, which dissolve readily in water and in alcohol, and effloresce slowly in the air. Heated to 100° the crystallized acid loses its water of crystallization; when subjected to the action of a stronger heat, it fuses at first, and afterwards carbonizes, with evolution of pungent acid fumes, the odor of which may be readily distinguished from that emitted by tartaric acid upon carbonization. By heating with

* Potassium or sodium tartrate dissolves calcium tartrate (as well as certain other salts insoluble in water, such as calcium phosphate, barium sulphate, etc.). Hence the alkali tartrate must be fully decomposed by the reagent.

a little nitric acid, citric acid gives oxalic and acetic acids; with much nitric acid it gives acetic acid only. Citric acid is tribasic.

2. The CITRATES with alkali base, whether normal or acid, are readily soluble in water; solution of citric acid therefore is not precipitated by potassium acetate. Various citrates containing weak bases, such as ferric citrate, for instance, are also freely soluble in water. Evaporated on the water-bath to syrupy consistence the solution of ferric citrate deposits no solid salt. Citrates, like tartrates, and for the same reason, prevent the precipitation of aluminic and ferric hydroxide, etc., by alkalies.

3. *Calcium chloride* fails to produce a precipitate in solution of free citric acid, even upon boiling; but a precipitate of NORMAL CALCIUM CITRATE $(C_6H_5O_7)_2Ca_3 . H_2O$ forms immediately upon saturating with potassa or soda the concentrated solution of citric acid, mixed with calcium chloride in excess.* The precipitate is insoluble in potassa, but dissolves freely in solution of ammonium chloride; upon boiling this ammonium chloride solution, normal calcium citrate separates again in the form of a white crystalline precipitate, which however is now no longer soluble in ammonium chloride. If a solution of citric acid mixed with excess of calcium chloride * is saturated with ammonia, a precipitate will form in the cold only after many hours' standing; but upon boiling the clear fluid, normal calcium citrate of the properties just stated will suddenly precipitate. By heating calcium citrate with ammonia and silver nitrate, the latter salt is not reduced, or only to a trifling extent.

4. *Lime water* added in excess * produces no precipitate in cold solutions of citric acid or of citrates. But upon boiling some time with a tolerable excess of hot prepared lime water, a white precipitate of CALCIUM CITRATE is formed, of which the greater portion redissolves upon cooling.

5. *Barium acetate* added in excess to a solution of an alkali citrate, whether hot or cold, produces an amorphous precipitate of the formula $(C_6H_5O_7)_2Ba_3 . 7H_2O$. Baryta water added in excess to citric acid produces the same precipitate.

* Alkali citrates are actual solvents for many compounds insoluble in water (barium sulphate, calcium phosphate, calcium oxalate, etc.) Hence the alkali citrate must be fully decomposed by the reagent.

The precipitate does not make its appearance in dilute solutions, because it is not insoluble in water, but if such solutions are heated, a precipitate separates which is first amorphous and soon turns to microscopic needles of the formula $(C_6H_5O_7)_2Ba_3 . 5H_2O$. On heating this or the amorphous salt with excess of barium acetate for two hours on the water-bath, another very characteristic salt is formed. The latter consists of well-formed clinorhombic prisms, and has the formula $(C_6H_5O_7)_2Ba_3 . 3\frac{1}{2}H_2O$. If the solution is very dilute, the salt does not form till after evaporation. This is an infallible reaction for citric acid * (H. KÄMMERER). From experiments made in my laboratory it appears that the addition of a drop of acetic acid materially assists the transition to the characteristic salt.

6. *Lead acetate* added in excess to a solution of citric acid produces a white amorphous precipitate of LEAD CITRATE, which after washing is readily soluble in ammonia free from carbonate. By digestion for several hours with water or acetic acid on a water-bath, the precipitate becomes crystalline, and then has the formula $(C_6H_5O_7)_2Pb_3 . 3H_2O$. The microscope does not reveal the presence of well-formed crystals.

7. *Silver nitrate* produces in solutions of normal citrates of the alkali metals a white flocculent precipitate of SILVER CITRATE, $C_6H_5O_7Ag_3$. On boiling a rather large quantity of this precipitate with a little water, a gradual decomposition sets in with separation of silver.

8. Upon heating citric acid or citrates with concentrated *sulphuric acid*, carbon monoxide and carbon dioxide escape at first, the sulphuric acid retaining its natural color; upon continued ebullition, however, the solution acquires a dark color, and sulphurous acid is evolved.

§ 165.

d. MALIC ACID, $C_2H_3(OH)(COOH)_2 = C_4H_6O_5$.

1. MALIC ACID crystallizes with difficulty, forming crystalline crusts, which deliquesce in the air, and dissolve readily in water and in alcohol. Exposed to a temperature of 140° malic acid is slowly converted, with loss of two molecules of water, into fumaric acid, $C_2H_2(COOH)_2 = C_4H_4O_4$; heated more strongly, malic acid is resolved into water and MALEIC ACID (isomeric with fumaric acid) which volatilizes. This deportment of malic acid is highly characteristic. If the

* The microscope is needed for identifying these crystals, which are figured in Fres. Zeitschrift, vol. 8, p. 299.

experiment is made in a small spoon, pungent acid vapors are evolved with frothing; if the experiment is made in a small tube, the maleic acid first, and afterwards the fumaric acid also will condense to crystals in the colder part of the tube. By heating with nitric acid, malic acid readily yields oxalic acid, with evolution of carbon dioxide.

2. Malic acid forms with most bases salts soluble in water. Hydrogen potassium malate is not difficultly soluble in water; potassium acetate fails therefore to precipitate solutions of malic acid. Malic acid prevents, like tartaric acid, the precipitation of ferric hydroxide, &c., by alkalies.

3. *Calcium chloride* added in excess fails to produce a precipitate in solutions of free malic acid. Even after saturation with ammonia or soda no precipitate is formed. But upon boiling, a precipitate of CALCIUM MALATE, $C_4H_4O_5Ca.H_2O$, separates from concentrated solutions. If the precipitate is dissolved in a very little hydrochloric acid, ammonia added to the solution, and the fluid boiled, the calcium malate separates again; but if it is dissolved in a somewhat larger quantity of hydrochloric acid, it will not reprecipitate, after addition of ammonia in excess, even upon continued boiling. On adding one or two measures of alcohol the calcium malate separates in white flocks. If the fluid is previously heated nearly to boiling and hot alcohol is added, the precipitate is deposited in the form of soft lumps which adhere to the sides of the vessel; on cooling they harden and crumble by pressure to a crystalline powder (BARFOED). When heated with ammonia and silver nitrate, calcium malate causes no separation of silver or hardly any.

4. *Lime water* produces no precipitate in solutions of free malic acid, nor in solutions of malates. The fluid remains perfectly clear even upon boiling, provided the lime water was prepared with boiling water.

5. *Lead acetate* throws down from solutions of malic acid and of malates a white precipitate of LEAD MALATE, $C_4H_4O_5Pb.3H_2O$. The precipitation is the most complete if the fluid is neutralized by ammonia, as the precipitate is slightly soluble in free malic acid and acetic acid, and also in ammonia. If the fluid in which the precipitate is suspended is heated to boiling, a portion of the precipitate dissolves, and the remainder fuses to a translucent mass resembling resin

melted under water, which on standing under the liquid gradually crystallizes. To obtain this reaction with small quantities, warm at first gently till the precipitate has shrunk together, then pour off the principal quantity of the fluid and heat the rest with the precipitate to boiling. This reaction is distinctly marked only if the lead malate is tolerably pure; if mixed with other lead salts—if, for instance, ammonia is added to alkaline reaction—it is only imperfect or fails altogether to make its appearance.

6. *Silver nitrate* throws down from solutions of normal malates of the alkali metals a white precipitate of SILVER MALATE which upon long standing or boiling turns a little gray.

7. On mixing the warm solution of free malic acid with *magnesia* or magnesium carbonate, till the acid reaction is destroyed, filtering, evaporating, and mixing the hot solution with hot alcohol, magnesium malate, $C_4H_4O_5Mg$, separates as a glutinous mass on the sides of the vessel. It is hard when cold. Malic acid cannot be distinguished from citric acid by this reaction (BARFOED).

8. Upon heating malic acid with concentrated *sulphuric acid*, carbon dioxide and carbon monoxide are evolved at first; the fluid then turns brown and ultimately black, with evolution of sulphur dioxide.

§ 166.

Recapitulation and remarks.—Of the organic acids of this group *oxalic acid* is characterized by the instant precipitation of its calcium salt from its solution in hydrochloric acid by ammonia, and also by sodium acetate, as well as by the immediate precipitation of the free acid by solution of calcium sulphate. *Tartaric acid* is characterized by the sparing solubility of the hydrogen potassium salt, the solubility of the calcium salt in cold solution of soda and potassa, the reaction of the calcium salt with ammonia and silver nitrate, and the peculiar odor which the acid and its salts emit upon heating. It is most safely detected in presence of the other acids by means of potassium acetate or potassium fluoride (§ 163, 4). C. D. BRAUN'S test for distinguishing tartaric acid from the other organic acids by means of hexamincobaltic chloride will be found in Zeitsch. f. anal. Chem. 7, 349. *Citric acid* is usually recognized by its reaction with lime water, or with calcium chloride and ammonia in presence of ammonium chloride; but in this we always presuppose the absence or the removal of malic and tartaric acids, and also the employment of a sufficient quantity of lime water or calcium chloride. A very

safe characteristic of citric acid also consists in the microscopic appearance of its barium salt (§ 164, 5). *Malic acid* would be sufficiently characterized by the deportment of lead malate when heated under water, were this reaction more sensitive, and not so easily prevented by the presence of other acids. The safest means of identifying malic acid is to convert it into maleic acid and fumaric acid by heating in a glass tube; but this conversion can be effected successfully only with pure malic acid. Lead malate is sparingly soluble in ammonia, whilst the citrate and tartrate of lead dissolve freely in that agent; this different deportment of the lead salts of the acids affords a means of distinguishing between them.

If only one of the four acids is present in a solution, lime water will suffice to indicate which of the four is present; since malic acid is not precipitated by this reagent, citric acid is precipitated only upon boiling, tartaric acid and oxalic acid being thrown down in the cold; and the calcium tartrate redissolves upon addition of ammonium chloride, whilst the oxalate does not.

If the four acids together are present in a solution, the oxalic acid and tartaric acid are usually precipitated first by calcium chloride and ammonia, in presence of ammonium chloride. But it must be noted here that the calcium tartrate requires some time for complete precipitation (it is separated from the oxalate by solution of soda), and also that alkali citrate when present in any quantity prevents the thorough separation of oxalic acid and still more of tartaric acid. On adding alcohol in moderate quantity cautiously to the filtrate, the calcium citrate separates (and with it the rest of the calcium oxalate and tartrate). On filtering again and mixing the filtrate with more alcohol, calcium malate is thrown down. From this the acid is prepared by dissolving it in acetic acid, adding alcohol, filtering if necessary, mixing the filtrate with lead acetate, neutralizing with ammonia, washing the precipitate, suspending it in water, treating with sulphuretted hydrogen, filtering and evaporating the filtrate to dryness. A better method for the detection of malic acid in the presence of the three other acids consists in combining the acids with ammonia, concentrating strongly, neutralizing the still warm fluid with ammonia (to dissolve the acid salts

produced in the evaporation) and adding 8 volumes of alcohol of 98 per cent. After 12 or 24 hours the solution of ammonium malate is filtered from the undissolved oxalate, tartrate, and citrate of ammonium, the malic acid is precipitated with lead acetate, and the pure acid is prepared from the precipitate (BARFOED). Where a small quantity of citric acid or malic acid is to be detected in presence of a large proportion of tartaric acid, the best way is to remove the latter first by potassium acetate, with addition of an equal volume of strong alcohol. The other acids may then be completely precipitated in the filtrate by excess of calcium chloride and ammonia if the quantity of the alcohol is a little increased.

§ 167.

RACEMIC ACID, $C_4 H_6 O_6$.

The formula of CRYSTALLIZED RACEMIC ACID is $C_4 H_6 O_6 . H_2 O$. The crystallization water escapes slowly in the air, but rapidly at 100° (difference between racemic acid and tartaric acid). To solvents the racemic acid comports itself like the tartaric acid. The RACEMATES also show very similar deportment to that of the tartrates. However, many of them differ in the amount of water they contain, and in form and solubility from the corresponding tartrates. The aqueous solution of racemic acid and the racemates exercises no diverting action upon polarized light. *Calcium chloride* precipitates from the solutions of free racemic acid and of racemates CALCIUM RACEMATE, $C_4 H_4 O_6 Ca . 4 H_2 O$, as a white crystalline powder. Ammonia throws down the precipitate from its solution in hydrochloric acid, either immediately or at least very speedily (difference between racemic acid and tartaric acid). It dissolves in solution of soda and potassa, but is reprecipitated from this solution by boiling (difference between racemic acid and oxalic acid). *Lime water* added in excess produces immediately a white precipitate insoluble in ammonium chloride (difference between racemic acid and tartaric acid). *Solution of calcium sulphate* does not immediately produce a precipitate in a solution of racemic acid (difference between racemic and oxalic acid); however after ten or fifteen minutes, calcium racemate separates (difference between racemic acid and tartaric acid); in solutions of normal racemates the precipitate forms immediately. With *potassium salts* racemic acid comports itself like tartaric acid. By letting sodium and potassium racemate or sodium and ammonium racemate crystallize, two kinds of crystals are obtained, which resemble each other as the image reflected by a mirror resembles the object reflected. The one kind of crystals contains common or dextro-tartaric acid (which turns the plane of polarized light towards the right); the other kind contains lævo-tartaric acid, *i.e.*, an acid which is the same in every respect as tartaric acid, with this exception only, that it turns the polarized light towards the left. If the two kinds of crystals are redissolved together, the solution shows again the reactions of the racemic acid.

Second Group.

THE ACIDS OF THE SECOND GROUP SUBLIME WITHOUT ALTERATION. BY HEATING WITH NITRIC ACID THEY ARE EITHER LEFT UNCHANGED (SUCCINIC ACID), OR MERELY CONVERTED INTO NITRO-ACID (BENZOIC ACID). THE CALCIUM SALTS ARE READILY SOLUBLE IN WATER (BENZOIC ACID), OR DIFFICULTLY SOLUBLE (SUCCINIC ACID). THE SOLUTIONS OF THE NORMAL ALKALI SALTS ARE PRECIPITATED BY FERRIC CHLORIDE: *Succinic Acid, Benzoic Acid.*

§ 168.

a. SUCCINIC ACID, $C_2H_4(COOH)_2 = C_4H_6O_4$.

1. SUCCINIC ACID forms colorless and inodorous prisms or tables (rhombic prisms or rhomboid tables). It has a slightly acid taste, is readily soluble in water and alcohol, slightly soluble in ether, difficultly soluble in nitric acid, and volatilizes when exposed to the action of heat, leaving only a little charcoal behind. The officinal acid has an empyreumatic odor, and leaves a somewhat larger carbonaceous residue upon volatilization. Succinic acid is not destroyed by heating with nitric acid, and may therefore be easily obtained in the pure state by boiling with that acid for half an hour, by which means the oil of amber, if present, will be destroyed. By sublimation crystalline needles of silky lustre are obtained. The acid loses water in this process, so that by repeated sublimation succinic anhydride is ultimately obtained. Heated in the air succinic acid burns with a blue flame, free from soot.

2. The SUCCINATES are decomposed at a red heat; those which have an alkali metal or alkali-earth metal for base are converted into carbonates with separation of charcoal. Most of the succinates are soluble in water. Sodium succinate is scarcely soluble in strong alcohol and crystallizes well both as normal and acid salt; hence it may be readily obtained in a pure state from very impure fluids. This property may be utilized for the detection and separation of the acid.* On heating the succinates with potassium disulphate in a tube, the acid sublimes. The acid may be also obtained from the salts by decomposing them with sulphuric acid, and extracting with warm absolute alcohol.

3. On mixing a cold neutral moderately dilute solution of an alkali succinate with *calcium chloride,* no precipitate is formed; on then adding alcohol a gelatinous precipitate of CALCIUM SUCCINATE falls, readily soluble in ammonium chloride. From this solution more alcohol reprecipitates the gelatinous salt; in case of great dilution no precipitate is produced at first, but in a short time the calcium succinate separates in the crystalline form, $C_4H_4O_4Ca.3H_2O$.

4. *Ferric chloride* produces in neutral solutions of the succinates of the alkali metals a brownish pale-red bulky precipitate of FERRIC SUCCINATE; some succinic acid is liberated in this reaction, and retains part of the precipitate in solution if the fluid is filtered off hot. The precipitate dissolves readily in mineral acids; ammonia decomposes it, causing the separation of a less bulky

* Compare MEISSNER and JOLLY, Zeitschr. f. anal. Chem., 4, 502.

precipitate of a highly basic ferric succinate, and combining with the greater portion of the acid to ammonium succinate, which dissolves.

5. *Lead acetate*, when added drop by drop to a solution of free succinic acid, or of an alkali succinate, produces a white amorphous precipitate which is immediately redissolved in excess of succinic acid, in alkali succinate, and in lead acetate, but in a short time separates from such solutions in the crystalline form. The precipitate consists of normal LEAD SUCCINATE, $C_4 H_4 O_4 Pb$; it is barely soluble in water, acetic acid, succinic acid, and lead acetate, readily soluble in nitric acid; by ammonia it is converted into a basic salt, $C_4 H_4 O_6 Pb$.

6. A mixture of *alcohol*, *ammonia* and *barium chloride* produces in solutions of free succinic acid and of succinates a white precipitate of BARIUM SUCCINATE, $C_4 H_4 O_4 Ba$.

§ 169.

b. BENZOIC ACID, $C_6 H_5 C O O H = C_7 H_6 O_2$.

1. Pure BENZOIC ACID forms inodorous white scales or needles, or simply a crystalline powder. It fuses when heated, and afterwards volatilizes completely. The fumes cause a peculiar irritating sensation in the throat, and provoke coughing; when cautiously cooled, they condense to brilliant needles; when kindled, they burn with a luminous sooty flame. The common officinal benzoic acid has the odor of benzoin, and leaves a small carbonaceous residue upon volatilization. Benzoic acid is very sparingly soluble in cold water, but it dissolves pretty freely in hot water and in alcohol. Addition of water imparts therefore a milky turbidity to a saturated solution of the acid in alcohol.

2. Most of the BENZOATES are soluble in water; only those with weak bases, *e.g.*, ferric benzoate, are insoluble. The soluble benzoates have a peculiar pungent taste. The addition of a *strong acid* to concentrated aqueous solutions of benzoates displaces the benzoic acid, which separates in the form of a dazzling white sparingly soluble powder. Benzoic acid is expelled in the same way from the insoluble benzoates by such strong acids as form soluble salts with the bases with which the benzoic acid is combined.

3. *Ferric chloride* precipitates solutions of free benzoic acid incompletely: neutral solutions of benzoates of the alkali metals completely. The precipitate of basic FERRIC BENZOATE is bulky, flesh colored, insoluble in water. It is decomposed by ammonia in the same manner as ferric succinate, from which salt it differs in this, that it dissolves in a little hydrochloric acid, with separation of the greater portion of the benzoic acid.

4. *Lead acetate* fails to precipitate free benzoic acid, but it produces flocculent precipitates in solutions of alkali benzoates. The precipitate is insoluble in sodium benzoate, but dissolves in lead acetate.

5. A mixture of *alcohol*, *ammonia* and *barium chloride* or *calcium chloride* produces no precipitate in solutions of benzoic acid or of the alkali benzoates.

§ 170.

Recapitulation and remarks.—Succinic and benzoic acids are distinguished from one another by the color of their ferric salts, and also by their different deportment with barium chloride or calcium chloride and alcohol; but prin-

cipally by their different degrees of solubility, succinic acid being readily soluble in water, whilst benzoic acid is very difficult of solution. Succinic acid is seldom perfectly pure, and may therefore often be detected by the odor of oil of amber which it emits.

The detection of the two acids, when present in the same solution with other acids, may be effected as follows: Precipitate with ferric chloride, warm the washed precipitate with ammonia, filter, concentrate the solution, divide it into two parts, and mix one part with hydrochloric acid, the other with barium chloride and alcohol.

Succinic acid and benzoic acid do not prevent the precipitation of ferric hydroxide, aluminium hydroxide, etc., by alkalies.

Third Group.

THE ACIDS OF THE THIRD GROUP MAY BE DISTILLED WITH WATER (LACTIC ACID WITH DIFFICULTY). THE CALCIUM SALTS ARE READILY SOLUBLE IN WATER. THE SOLUTIONS OF THE NORMAL ALKALI SALTS ARE NOT PRECIPITATED IN THE COLD BY FERRIC CHLORIDE: *Acetic acid*, *Formic acid* (Lactic Acid, Propionic Acid, Butyric Acid).

§ 171.

a. ACETIC ACID, $CH_3COOH = C_2H_4O_2$.

1. ACETIC ACID forms transparent crystalline scales, which fuse at 17° to a colorless fluid of a peculiar pungent and penetrating odor, and exceedingly acid taste. When exposed to the action of heat, it volatilizes completely, forming pungent vapors, which burn with a blue flame. It is miscible with water in all proportions; it is to such mixtures of the acid with water that the name of acetic acid is commonly applied. Acetic acid is also soluble in alcohol.

2. The ACETATES undergo decomposition at a red heat; among the products of this decomposition we generally find acetic acid, and almost invariably acetone, $CO(CH_3)_2$. The acetates of the alkali metals and alkali-earth metals are converted into carbonates in this process; of the other metallic acetates many leave the metal behind in the pure state, others in the form of oxides. Most of the residues which the acetates leave upon ignition are carbonaceous. Nearly all acetates dissolve in water and in alcohol; most of them are readily soluble in water, a few only are difficult of solution in that

menstruum. If acetates are distilled with dilute sulphuric acid, the free acetic acid is obtained in the distillate.

3. If *ferric chloride* is added to acetic acid, and the acid is then nearly saturated with ammonia, or if a neutral acetate is mixed with ferric chloride, the fluid acquires a deep red color, owing to the formation of FERRIC ACETATE. By boiling the fluid becomes colorless if it contains an excess of acetate, the whole of the iron precipitating as a basic acetate, in the form of brown-yellow flakes. Ammonia precipitates from it the whole of the iron as hydroxide. By addition of hydrochloric acid a fluid which appears red from the presence of ferric acetate turns yellow (difference from ferric sulphocyanate).

4. Neutral acetates (but not free acetic acid of a certain degree of dilution) give with *silver nitrate* white crystalline precipitates of SILVER ACETATE, $C_2H_3O_2Ag$, which are very sparingly soluble in cold water. They dissolve more easily in hot water, but separate again upon cooling, in the form of very fine crystals. Ammonia dissolves them readily; free acetic acid does not increase their solubility in water.

5. *Mercurous nitrate* produces in acetic acid, and more readily still in acetates, white scaly crystalline precipitates of MERCUROUS ACETATE $(C_2H_3O_2)_2Hg_2$ which are sparingly soluble in water and acetic acid in the cold, but dissolve without difficulty in an excess of the precipitant. The precipitates dissolve in water upon heating, but separate again upon cooling, in the form of small crystals; in this process the salt undergoes partial decomposition; a portion of the mercury separates in the metallic state, and imparts a gray color to the precipitate. If the mercurous acetate is boiled with dilute acetic acid, instead of water, the quantity of the metallic mercury which separates is exceedingly minute.

6. *Mercuric chloride* produces no precipitate of mercurous chloride with acetic acid or acetates upon heating.

7. By heating acetates with *concentrated sulphuric acid*, ACETIC ACID is evolved, which may be known by its pungent odor. But if the acetates are heated with a mixture of about equal volumes of *concentrated sulphuric acid* and *alcohol*, ETHYL ACETATE, $C_2H_5C_2H_3O_2$, is formed. The odor of this ether is highly characteristic and agreeable; it is most distinct upon shaking the mixture when somewhat cooled, and is much less liable to lead to mistakes than the pungent odor of the acid.

8. If dilute acetic acid is heated with an excess of *lead oxide*, part of the latter dissolves as triplumbic diacetate. The fluid has an alkaline reaction; it gives no crystals on cooling.

§ 172.

b. Formic Acid, $HCOOH = CH_2O_2$.

1. Formic acid is a transparent and colorless slightly fuming liquid of a characteristic and exceedingly penetrating odor. When cooled to below 0°, it crystallizes in colorless plates. It is miscible in all proportions with water and alcohol. When exposed to the action of heat, it volatilizes completely; the vapors burn with a blue flame.

2. The formates, like the corresponding acetates, leave upon ignition either carbonates, oxides, or metals behind, the process being attended with separation of charcoal, and escape of carbon dioxide and water. All the compounds of formic acid with bases are soluble in water; alcohol also dissolves many of them, but not all.

3. Formic acid shows the same reaction with *ferric chloride* as acetic acid.

4. *Silver nitrate* fails to precipitate free formic acid, and decomposes the alkali formates only in concentrated solutions. The white, sparingly soluble, crystalline precipitate of silver formate, CHO_2Ag, acquires very rapidly a darker tint, owing to the separation of metallic silver. Complete reduction of the silver to the metallic state takes place, even in the cold, after the lapse of some time; but immediately upon applying heat to the fluid containing the precipitate. The same separation of metallic silver takes place in a solution of free formic acid, and also in solutions of formates so dilute that the addition of the silver nitrate fails to produce a precipitate. But it does not take place in presence of an excess of ammonia.

5. *Mercurous nitrate* gives no precipitate with free formic acid; but in solutions of alkali formates this reagent produces a glistening white sparingly soluble precipitate of mercurous formate $(CHO_2)_2Hg_2$, which rapidly becomes gray, owing to the separation of metallic mercury. Complete reduction ensues, even in the cold, after the lapse of some time, but is immediate upon application of heat. This reduction is also attended with the formation of carbon dioxide and water, and takes place both in solutions of free formic acid and in fluids so highly dilute that the mercurous formate is retained in solution.

6. If formic acid or an alkali formate is heated with *mercuric chloride* to between 60° and 70°, mercurous chloride precipitates. Presence of free hydrochloric acid or of somewhat considerable quantities of alkali chlorides prevent the reaction.

7. If formic acid or a formate is heated with *concentrated sulphuric acid*, the formic acid is resolved into water and carbon monoxide gas, which latter escapes with effervescence and, if kindled, burns with a blue flame. The fluid does not turn black in this process, $CH_2O_2 = CO + H_2O$. Upon heating formates with dilute sulphuric acid in a distilling apparatus free formic acid is obtained in the distillate, and may mostly be readily detected by its odor. Upon heating a formate with a mixture of strong sulphuric acid and alcohol, ethyl formate is evolved, which is characterized by its peculiar rum-like smell.

8. If dilute formic acid is heated with excess of *lead oxide*, the latter partially dissolves. The fluid has an alkaline reaction. On cooling the solution, which, if necessary, is concentrated by evaporation, lead formate $(CHO_2)_2Pb$, separates in brilliant prisms or needles.

§ 173.

Recapitulation and Remarks.—Acetic acid and formic acid may be distilled over with water, and form with quadrivalent iron soluble neutral salts which dissolve in water, with a blood-red color, and are decomposed upon boiling. These reactions distinguish the two acids of the third group from the other organic acids. From each other the two acids are distinguished by their odor and the odor of their ethyl compounds, and by their different reactions with silver salts and salts of mercury, with lead oxide and concentrated sulphuric acid. The separation of acetic acid from formic acid is effected by heating the mixture of the two acids with an excess of mercuric oxide or argentic oxide. Formic acid reduces the oxide, and suffers decomposition whilst the acetic acid dissolves the oxide and remains in solution as an acetate.

§ 174.

Rarer Acids of the Third Group.

1. LACTIC ACID, $C_3 H_6 O_3$.*

Lactic acid is developed in animal fluids, vegetable matters that have turned sour, etc. Lactic acid is a colorless syrupy liquid; it has a pure acid, sharp taste. When it is slowly heated in a retort to 130°, water containing a little lactic acid distils over, leaving a residue of lactic anhydride, $C_6 H_{10} O_5$, which between 250° and 300° is decomposed into carbon monoxide, lactide, $C_3 H_4 O_2$, and other products. Lactic acid dissolves freely in water, alcohol, and ether. Upon boiling the aqueous solution, a little lactic acid volatilizes with the aqueous vapor. All the lactates are soluble in water and alcohol, the greater part of them, however, only sparingly; they are all insoluble in ether. The production of some of these salts and the examination of their form under the microscope supply the means for the detection of lactic acid; calcium lactate and zinc lactate are the best suited for this purpose. Calcium lactate may be conveniently prepared from animal or vegetable juices by the following method devised by SCHERER: Dilute the liquid, if necessary, with water, mix with baryta water, and filter. Distil the filtrate with some sulphuric acid (to remove volatile acids), digest the residue several days with strong alcohol, distil the acid solution with a little milk of lime, filter warm from the excess of lime and calcium sulphate, conduct carbon dioxide into the filtrate, heat once more to boiling, filter from the precipitated calcium carbonate, evaporate the filtrate,

* Four isomeric lactic acids are now believed to exist. That produced in fermentation, or *Ethylidene lactic acid*, and the two existing together in the juice of flesh, viz., *Ethylene lactic acid* and *Paralactic acid*, agree quite closely in general properties.

warm the residue with strong alcohol, filter, and let the neutral filtrate stand several days to give the calcium lactate time to crystallize. Should the quantity of lactic acid present be insufficient to allow the formation of crystals, evaporate the fluid to syrupy consistence, mix with strong alcohol, let the mixture stand some time, decant or filter the alcoholic solution into a vessel that can be closed, and add gradually a small quantity of ether. This process will cause even minute traces of calcium lactate to separate from the fluid. Calcium lactate shows under the microscope the form of minute crystalline needles aggregated in tufts with short stalks, pairs of them always being joined at the stalked ends, so as to look like paint-brushes united together. Zinc lactate deposited quickly from its solution shows under the microscope the form of spherical groups of needles. The slow evaporation of solution of zinc lactate gives first crystals resembling clubs truncated at both ends; these crystals gradually increase in size; the two ends apparently diminish, whilst the middle parts increase in size (FUNKE).

2. PROPIONIC ACID, $C_2H_5COOH = C_3H_6O_2$, and 3. BUTYRIC ACID, $C_3H_7COOH = C_4H_8O_2$.*

PROPIONIC ACID is formed under a great variety of circumstances; it is chiefly found in fermented liquids. The pure acid crystallizes at low temperature; it boils at 140.5°; it dissolves readily in water. Propionic acid floats as an oily stratum on concentrated aqueous solutions of phosphoric acid and on solution of calcium chloride. It has a peculiar smell, which reminds both of butyric and acetic acid. Upon distilling the aqueous solution, the propionic acid passes over into the distillate. NORMAL BUTYRIC OR ETHACETIC ACID ($CH_3.CH_2.CH_2.COOH$) is frequently found in animal and vegetable matter, more particularly also in fermented liquids of various kinds. The pure acid is a colorless, mobile, corrosive, intensely sour fluid, of a disagreeable odor, a combination of the smell of rancid butter and acetic acid; it boils at 163°. It is miscible in all proportions with water and alcohol. It is separated from the concentrated aqueous solution by calcium chloride, concentrated acids, etc., in the form of a thin oil. The smell of butyric acid is particularly strong in the aqueous solution of the acid. Upon distilling the aqueous solution, the acid passes over with the aqueous vapors. Calcium butyrate is less soluble in hot than in cold water.

Propionic acid and butyric acid are often found associated with formic acid and acetic acid in fermented liquids, in guano, and in many mineral waters. The detection of the several acids may in such cases be effected as follows: Dilute the substance sufficiently with water, acidify with sulphuric acid, and distil; saturate the distillate with baryta water, evaporate to dryness, and treat the residue repeatedly with boiling alcohol of 85 per cent. This will leave the barium formate and part of the barium acetate, the remainder of the acetate, together with the propionate and butyrate, dissolving in the alcohol. Evaporate the alcoholic solution, dissolve the residue in water, decompose cautiously with silver

* *Normal butyric acid* and *isobutyric* or *dimethacetic acid* $(CH)(CH_3)_2(COOH)$ have the same compositions and nearly the same properties. The reactions above given are those of the normal and most commonly occurring acid. Isobutyric acid, existing in the carob bean, boils at 154°; its calcium salt is more soluble in hot than cold water.

sulphate, boil, filter, and let the fluid (which ought rather to contain a little undecomposed barium salt than any silver sulphate), evaporate under the desiccator. Take out separately the crystals which form first, those which form after, and those which form last, and examine them to ascertain their nature. Silver acetate emits upon solution in concentrated sulphuric acid the odor of acetic acid, and gives no oily drops; silver propionate and butyrate emit the peculiar odor of the acids, and give oily drops, which, however, with minute quantities are visible only under the microscope. To distinguish positively between propionic and butyric acid, it is indispensable to determine the amount of silver in the separated silver salts, and to fix by this the molecular weight of the acids. If much barium acetate has passed into the solution, with a small quantity only of butyrate and propionate, the barium is first exactly precipitated with sulphuric acid from the aqueous solution of the barium salts soluble in alcohol, half of the acid fluid neutralized with soda, the other half added, the fluid then distilled, the distillate, which now contains principally propionic and butyric acids, saturated with baryta, then decomposed with silver sulphate, and the remaining part of the process conducted as above.

PART II.

SYSTEMATIC COURSE

OF

QUALITATIVE CHEMICAL ANALYSIS.

PRELIMINARY REMARKS.

THE knowledge of reagents and of the deportment of bodies with them enables us to ascertain at once whether a compound, of which the physical properties permit an inference as to its nature, is in reality what we suspect it to be. Thus, for instance, a few simple reactions suffice to show that a body which appears to be calcite is really calcium carbonate, and that another which we hold to be gypsum is actually calcium sulphate. This knowledge usually suffices also to ascertain whether a certain body is present or not in a mixture; for instance, whether or not a white powder contains mercurous chloride. But if our design is to ascertain the chemical nature of a substance entirely unknown to us—if we wish to discover *all* the constituents of a mixture or chemical compound—if we intend to prove that, besides certain bodies which we have detected, no other substance *can* possibly be present—if consequently a *complete* qualitative analysis is our object, the mere knowledge of the reagents, and of the reactions of bodies with them, will not suffice for the attainment of this end; this requires the additional knowledge of a *systematic course* of analysis, in other words, the knowledge of the *order* in which solvents, and general and special reagents, should be applied, both to effect the speedy and certain detection of every element present, and to prove with certainty the absence of all others. If we do not possess the knowledge of this systematic course, or if, in the

hope of attaining our object more rapidly, we adhere to no method, analyzing becomes (at least in the hands of a novice) mere guess-work, and the results obtained are no longer the fruits of scientific calculation, but mere matters of accident, which sometimes may prove lucky hits, and at others total failures.

Every analytical investigation must therefore be based upon a definite method. But it is not by any means necessary that this method should be the same in all cases. Practice, reflection, and a due attention to circumstances will, on the contrary, generally lead to the adoption of different methods for different cases. However, all analytical methods agree in this, that the substances to be looked for are in the first place classed into groups, which are then again subdivided, until the individual detection of the various substances present is finally accomplished. The diversity of analytical methods depends partly on the order in which reagents are applied, and partly on their selection.

Before we can venture upon inventing methods of our own for individual cases, we must first make ourselves thoroughly conversant with a course of chemical analysis in general. This system must have passed through the ordeal of experience, and must be adapted to every imaginable case, so that afterwards, when we have acquired some practice in analysis, we may be able to determine which modification of the general method will be best adapted to a given case.

The exposition of such a systematic course, adapted to all cases, tested by experience, and combining simplicity with the greatest possible security, is the object of the *First Section*.

The elements and compounds comprised in it are the same which we have studied in Part I., with the exception of those discussed more briefly, and marked by the use of smaller type.

The subdivisions of this systematic course are, 1, Preliminary Examination; 2, Solution; 3, Actual Analysis.

The third subdivision (the *Actual Analysis*) is adapted for the full investigation of any mixture or compound in which all the substances treated in the present work may be present. With respect to the latter I have to remark that where the preliminary examination has not clearly demonstrated the

absence of certain groups of substances, the student cannot safely disregard any of the paragraphs to which reference is made, in consequence of the reactions he has observed. In cases where the intention is simply to test a mixture for certain substances, and not to ascertain all its constituents, it will be easy to select the particular paragraphs which ought to be attended to.

As the construction of a universally applicable systematic course of analysis requires due provision for every contingency that may possibly arise, it is self-evident that, though in the system here laid down the various bodies comprised in it have been assumed to be mixed up together in every conceivable way, it was absolutely indispensable to assume that no foreign *organic matters* were present, since the presence of such matters would introduce various complications.

Although the general analytical course laid down here is devised and arranged in a manner to suit all possible contingencies, still there are special cases in which it may be advisable to modify it. A preparatory treatment of the substance is also sometimes necessary, before the actual analysis can be proceeded with; the presence of coloring or slimy organic matters more especially requires certain preliminary operations. The *Second Section* will be found to contain a detailed description of the special methods employed to meet certain cases which frequently occur. Some of these methods show how the analytical process becomes simplified as the number of substances decreases to which regard must be had.

In conclusion, as an intelligent and successful pursuit of analysis is possible only with an accurate knowledge of the principles whereon the detection and separation of bodies depend, I have given in the *Third Section* an explanation of the general analytical process, with numerous additions to the practical operations. As this third section may properly be regarded as the key to the first and second sections, I strongly recommend students to make themselves early and thoroughly acquainted with it. I have devoted a special section to this theoretical explanation, as I think it will be understood better in a connected form than it would have been by explanatory additions to the several paragraphs, which, moreover, might have materially interfered with the perspicuity of the practical process.

I have also in this third section taken occasion to point out in what residues, solutions, precipitates, etc., which are obtained in the systematic course of analysis, the *rarer elements*, *acids*, or *radicals* may be expected to be met with; and also to give instructions how to proceed with a view to insure the detection of these bodies also systematically.

Finally, the student should, at the outset of his analytical work, form the habit of keeping a full and systematic record of his results, and of every item of experience which it may be useful to refer to. See Appendix III.

SECTION I.

PRACTICAL PROCESS FOR THE ANALYSIS OF COMPOUNDS AND MIXTURES IN GENERAL.

I. Preliminary Examination.

☞ *Do not fail to consult the observations in the Third Section of Part II., page* 415.

§ 175.

Examine, in the first place, the external properties, such 1*
as the color, shape, hardness, gravity, odor, etc., of the substance, since these will often enable you in some measure to infer its nature. Before proceeding, if the quantity of the substance is limited, you must consider how much may safely be spared for the preliminary examination. A reasonable economy is in all cases advisable, even though you may possess the substance in large quantities; but, under all circumstances, let it be a fixed rule never to use up the whole of what you possess of a substance, but always to keep a portion of it for unforeseen contingencies, and for confirmatory experiments.

For a general view of the subdivisions of the Course of Analysis, see the Table of Contents of Part II., at the beginning of the book.

* These marginal numbers are simply intended to facilitate reference.

A. The Body under Examination is Solid.

I. It is neither a Metal nor an Alloy.

§ 176.

1. The substance is fit for examination if in powder or in minute crystals; but in the case of larger crystals or solid pieces, a portion must, if practicable, be first reduced to *fine powder*. Bodies of the softer kind may be triturated in a porcelain mortar; those of a harder nature must first be broken into small pieces in a steel mortar, or upon a steel anvil, and the pieces then be triturated in an agate mortar. 2

2. Put some of the powder into a glass tube, sealed at one end, about 2 inches long and $\frac{3}{16}$ths of an inch wide, and heat first gently over the spirit or gas lamp, then intensely in the blowpipe flame. The reactions resulting may lead to many positive or probable conclusions regarding the nature of the substance. The following are the most important of these reactions, to which particular attention ought to be paid; it often occurs that several of them are observed in the case of one and the same substance: 3

a. The substance remains unaltered: absence of organic matters, salts containing water of crystallization, readily fusible matters, and volatile bodies (except carbon dioxide, which often escapes without visible change). 4

b. The substance does not fuse at a moderate heat, but simply changes color. From white to yellow, turning white again on cooling, indicates zinc oxide; from white to yellowish brown, turning to a dirty light yellow on cooling, indicates stannic oxide; from white or yellowish-red to brownish-red, turning to yellow on cooling, the body fusing at a red heat, indicates lead oxide; from white, or pale-yellow, to orange-yellow, up to reddish-brown, turning pale-yellow on cooling, the body fusing at an intense red heat, indicates bismuth trioxide; from brownish-red to black, turning brownish-red again on cooling, indicates ferric oxide; from yellow to dark-orange, the 5

body fusing at an intense heat, indicates POTASSIUM CHROMATE, etc.

c. THE SUBSTANCE FUSES WITHOUT EXPULSION OF AQUEOUS VAPORS. If, by intense heating, gas (oxygen) is evolved, and a small fragment of charcoal thrown in is energetically consumed, NITRATES or CHLORATES are indicated. 6

d. AQUEOUS VAPORS ARE EXPELLED, WHICH CONDENSE IN THE COLDER PART OF THE TUBE: this indicates either (α) SUBSTANCES CONTAINING CRYSTAL WATER, in which case they will generally readily fuse, and resolidify after expulsion of the water; many of these swell considerably whilst yielding up their water, *e. g.*, borax, alum; or (β) decomposable HYDROXIDES, in which case the bodies often will not fuse; or (γ) anhydrous salts, holding WATER MECHANICALLY ENCLOSED between their lamellæ, in which case the bodies will decrepitate; or (δ) bodies with MOISTURE externally adhering to them. 7

Test the reaction of the condensed fluid in the tube; if it is alkaline, ammonia is indicated; if acid, a volatile acid (sulphuric, sulphurous, hydrofluoric, hydrochloric, hydrobromic, hydriodic, nitric, etc.).

e. GASES OR FUMES ESCAPE. Observe whether they have a color, a smell, an acid or alkaline reaction, whether they are inflammable, etc. 8

aa. OXYGEN indicates metallic dioxides, chlorates, nitrates, etc. A glimmering slip of wood is relighted in the gaseous current.

bb. SULPHUR DIOXIDE is often produced by decomposition of sulphates; it may be known by its odor and by its acid reaction with moist blue litmus paper.

cc. NITRYL (NO_2), resulting from the decomposition of nitrates, especially those of the heavy metals; it may be known by the brownish-red color and the odor of the fumes.

dd. CARBON DIOXIDE indicates carbonates decomposable by heat, or oxalates of reducible metals, or if accompanied by carbonization (see **10**) organic bodies. The gas is colorless and tasteless, noninflammable; a drop of lime water on a watch glass

becomes turbid on exposure to the gaseous current.

ee. CARBON MONOXIDE indicates oxalates and also formates. The gas burns with a blue flame. In the case of oxalates the carbon monoxide is generally mixed with carbon dioxide, and is therefore more difficult to kindle: in the case of formates there is marked carbonization. Oxalates evolve carbon dioxide when brought into contact with manganese dioxide, a little water, and some concentrated sulphuric acid, on a watch glass; formates evolve no carbon dioxide under similar circumstances.

ff. CHLORINE, BROMINE, or IODINE indicate decomposable chlorides, bromides, or iodides. The gases are readily recognized by their color and odor. Iodine, if evolved in any quantity, forms a black sublimate (compare **9**).

gg. CYANOGEN indicates cyanides decomposable by heat. The gas may be known by its odor, and, when tolerably pure, by the crimson flame with which it burns.

hh. HYDROSULPHURIC ACID indicates sulphides containing water; the gas may be readily known by its odor.

ii. AMMONIA, resulting from the decomposition of ammonium salts, or also of cyanides or nitrogenous organic matters, in which latter cases browning or carbonization takes place, and either cyanogen or offensive empyreumatic oils escape with the ammonia.

f. A SUBLIMATE FORMS. This indicates volatile bod- **9**
ies: the following are those more frequently met with:—

aa. SULPHUR. Eliminated from mixtures or from many of the metallic sulphides. Sublimes in reddish brown drops, which solidify on cooling, and turn yellow or yellowish-brown.

bb. IODINE. Eliminated from mixtures, many iodides, iodic acid, etc. Violet vapor, black sublimate, smell of iodine.

cc. AMMONIUM SALTS give white sublimates; heated

with sodium carbonate and a drop of water on platinum foil they evolve ammonia.

dd. MERCURY and its compounds. METALLIC MERCURY forms globules; MERCURIC SULPHIDE is black, but acquires a red tint when rubbed; MERCURIC CHLORIDE fuses before volatilizing; MERCUROUS CHLORIDE sublimes without previous fusion, the sublimate, which is yellow whilst hot, turns white on cooling. The red MERCURIC IODIDE gives a yellow sublimate.

ee. ARSENIC and its compounds. METALLIC ARSENIC forms the well-known arsenical mirror; ARSENIOUS OXIDE forms small shining crystals; the SULPHIDES OF ARSENIC give sublimates which are reddish yellow whilst hot, and turn yellow on cooling.

ff. ANTIMONIOUS OXIDE fuses to a yellow liquid before subliming. The sublimate consists of brilliant needles.

gg. BENZOIC ACID and SUCCINIC ACID. The officinal impure acids may be known by the odor of their fumes.

hh. OXALIC ACID. White crystalline sublimate, thick irritating fumes in the tube. Heating a small sample on platinum foil with a drop of concentrated sulphuric acid gives rise to a copious evolution of gas.

g. CARBONIZATION TAKES PLACE: organic substances. 10
This is always attended with evolution of gases (acetates evolve acetone) and water, which latter has an alkaline or acid reaction. If the residue effervesces with acids, whilst the original substance did not show this reaction, organic acids may be assumed to be present in combination with alkali or alkali-earth metals. Salts containing readily reducible metals in combination with organic acids often leave the metal behind, with little or no carbon. [Since the observations suggested by this paragraph will decide the operator whether or not to look for an organic acid in the subsequent analysis, it may be well to caution the beginner not to be too hasty in concluding that carbonization does or does not occur. In addition to what is stated above, we may mention that: 1. *Black-*

ening is not necessarily carbonization, for salts of volatile acids with certain metals, as copper, nickel, and cobalt, blacken on ignition from separation of the oxide. 2. Carbonization, *i.e.*, the separation of carbon, is usually attended with the disengagement of vapors, which often condense in oily droplets, or as an oily film on the cold part of the tube, and which have a "burnt" odor. 3. The carbon remaining after these vapors cease to escape usually takes fire when heated in contact with the air, and *glows* with red heat until it is consumed. 4. Carbonization is, in general, best observed when the body is heated *rapidly* to a high temperature.—ED.]

3. PLACE A SMALL PORTION OF THE SUBSTANCE ON A CHARCOAL SUPPORT (in the cavity scooped out for the purpose), AND EXPOSE TO THE INNER BLOWPIPE FLAME. **11**

As most of the reactions described under 2 (**3–10**) are also produced by this process, only those appearances will be mentioned which are peculiar to this experiment. Evolution of sulphur dioxide, when the flame plays upon the sample, generally indicates a sulphide. The following are the reactions which will permit pretty accurate conclusions:

a. THE BODY FUSES, AND IS ABSORBED BY THE CHARCOAL OR FORMS A BEAD IN THE CAVITY, not attended by incrustation: indicates more particularly salts of the alkali metals. **12**

b. AN INFUSIBLE WHITE RESIDUE REMAINS on the charcoal, either at once or after previous melting in the water of crystallization; consists of or indicates more particularly the oxides of barium, strontium, calcium, magnesium, aluminium, zinc (appears yellow whilst hot), and silicic oxide. Among these substances the OXIDES of STRONTIUM, CALCIUM, MAGNESIUM, and ZINC are distinguished by strong luminosity in the blowpipe flame. Moisten the white residue with a drop of cobalt nitrate, and expose again to a strong heat. A fine blue tint indicates ALUMINIUM; a green, ZINC. In the presence of SILICIC OXIDE and of many PHOSPHATES of the alkali-earth metals a more or less blue coloration is produced with partial fusion. **13**

In the case *a* or *b* the preliminary examination for alkali and alkali-earth metals may be completed by inspecting the colors which the substances impart to flame. For this purpose a little of the substance is attached to the loop of a fine platinum wire, moistened repeatedly with sulphuric acid, dried cautiously near the border of the flame, and then held in the fusing zone of BUNSEN'S gas flame. The colorations caused by the alkali metals will make their appearance first, followed—after volatilization of the alkali metals, by that of barium, and finally—after moistening with hydrochloric acid—by those of strontium and calcium. For details see § 92 and § 99.

c. THE SUBSTANCE LEAVES A RESIDUE OF ANOTHER COLOR, OR REDUCTION TO THE METALLIC STATE TAKES PLACE, OR AN INCRUSTATION FORMS ON THE CHARCOAL. Mix a portion of the powder with sodium carbonate and a drop of water, and heat on charcoal in the reducing flame; observe the residue in the cavity as well as the incrustation on the charcoal. 14

α. The sustained application of a strong flame produces a metallic globule, without incrustation of the charcoal, indicates GOLD OR COPPER. The latter is at once recognized by the green coloration of the flame. The compounds of platinum, iron, cobalt, and nickel are indeed also reduced, but they yield no metallic globules. 15

β. The charcoal support is coated with an incrustation, either with or without formation of a metallic globule. 16

aa. The incrustation is *white*, at some distance from the test specimen, and is very readily dissipated by heat, emitting a garlic-like odor: ARSENIC.

bb. The incrustation is *white*, nearer the test specimen than in *aa*, and may be driven from one part of the support to another: ANTIMONY. Metallic globules are generally observed at the same time, which continue to evolve white fumes long after the blowpipe jet is discontinued, and upon cooling become surrounded with crystals of antimonious oxide; the globules are brittle.

cc. The incrustation is *yellow* whilst hot, but turns white on cooling; it is pretty near the test specimen and is with difficulty volatilized: ZINC.

dd. The incrustation has a *faint yellow* tint whilst hot, but turns white on cooling; it surrounds the test specimen closely, and both the inner and outer flame fail to volatilize it: TIN. The metallic globules formed at the same time, but only in a strong reducing flame, are bright, readily fusible, and malleable.

ee. The incrustation has a *lemon-yellow* color, turning on cooling to sulphur-yellow; heated in the reducing flame it volatilizes, tinging the flame blue: LEAD. Readily fusible, malleable globules are formed at the same time with the incrustation.

ff. The incrustation is of a *dark orange-yellow* color whilst hot, which changes to lemon-yellow on cooling; heated in the reducing flame it changes its place without coloring the flame: BISMUTH. The metallic globules formed at the same time as the incrustation are readily fusible and brittle.

gg. The incrustation is reddish brown, in thin layers orange-yellow; it volatilizes without coloring the flame: CADMIUM.

hh. The incrustation is dark red: SILVER. Where lead and antimony are present at the same time, the incrustation is crimson.

To learn, in cases of doubt, whether reduced metal has been separated in this experiment, the charcoal cavity is moistened with water, the charcoal cut out for a little space around and below the cavity, brought into an agate mortar, finely pulverized, and the charcoal powder cautiously washed away. Any metal that may be present remains in the mortar, gold in yellow, copper in red, silver in white, tin in grayish white, lead in gray plates or streaks. Bismuth will remain as a reddish-gray, zinc a bluish-gray, antimony a gray powder. When copper and tin or copper and zinc are simultaneously present, yellow alloys

of these metals may be formed. [Iron, nickel, and cobalt, when reduced on charcoal, remain after washing as black or dark-gray powders, which are lifted by the magnet.]

4. FUSE A SMALL PORTION WITH A BEAD OF SODIUM METAPHOSPHATE AND EXPOSE FOR SOME TIME TO THE OUTER FLAME OF THE BLOWPIPE. 17

a. THE SUBSTANCE DISSOLVES READILY AND COPIOUSLY TO A CLEAR BEAD (WHILST HOT).

α. The hot bead is colored: 18

BLUE, by candlelight inclining to violet—COBALT;

GREEN, upon cooling blue; in the reducing flame, after cooling, red—COPPER;

GREEN, particularly fine on cooling, unaltered in the reducing flame—CHROMIUM;

BROWNISH-RED, on cooling, light-yellow or colorless; in the reducing flame, red whilst hot, yellow whilst cooling, then greenish—IRON;

REDDISH TO BROWNISH-RED, on cooling yellow to reddish-yellow or colorless; in the reducing flame, unaltered—NICKEL;

YELLOWISH-BROWN, on cooling, light-yellow or colorless; in the reducing flame almost colorless (especially after addition of a very little tin), blackish-gray on cooling—BISMUTH;

LIGHT-YELLOWISH to OPAL, when cold rather dull; in the reducing flame whitish-gray—SILVER;

AMETHYST-RED, especially on cooling; colorless in the reducing flame, not quite clear—MANGANESE.

β. The hot bead is colorless: 19

IT REMAINS CLEAR ON COOLING: ANTIMONY, ALUMINIUM, ZINC, CADMIUM, LEAD, CALCIUM, MAGNESIUM; the latter five, when added in somewhat large proportion to the sodium metaphosphate, give enamel-white beads; the bead saturated with lead is yellowish;

IT BECOMES ENAMEL-WHITE ON COOLING, EVEN WHERE ONLY A SMALL PORTION OF THE POWDER HAS BEEN ADDED TO THE SODIUM METAPHOSPHATE: BARIUM, STRONTIUM.

b. THE SUBSTANCE DISSOLVES SLOWLY AND ONLY IN SMALL QUANTITY: 20

α. The bead is colorless, and remains so even after cooling; the undissolved portion looks semi-transparent; upon addition of a little ferric oxide it acquires the characteristic color of an iron bead: SILICIC OXIDE.

β. The bead is colorless, and remains so after addition of a little ferric oxide: TIN.

c. THE SUBSTANCE DOES NOT DISSOLVE, BUT FLOATS (IN THE METALLIC STATE) IN THE BEAD: GOLD, PLATINUM. 21

5. MINERALS ARE EXAMINED FOR FLUORINE AS DIRECTED § 146, 8.

As the body under examination may consist of a mixture of the most dissimilar elements, reactions may be observed in an experiment which proceed from a combination of two or several cases. Such reactions must of course be interpreted accordingly.

After the termination of the preliminary examination, proceed to the solution of the substance, as directed § 180 (32).

§ 177.

II. THE SUBSTANCE IS A METAL OR AN ALLOY.

1. HEAT A SMALL PORTION OF THE SUBSTANCE WITH WATER ACIDULATED WITH ACETIC ACID. If HYDROGEN is evolved this indicates a light metal (possibly also manganese). 22

2. HEAT A SAMPLE OF THE SUBSTANCE ON CHARCOAL IN THE REDUCING FLAME OF THE BLOWPIPE, and watch the reactions; for instance, whether the substance fuses, whether an incrustation is formed, or an odor emitted, etc. 23

By this operation the following metals may be detected with more or less certainty: ARSENIC by the smell of garlic; MERCURY by its volatility; ANTIMONY, ZINC, LEAD, BISMUTH, CADMIUM, TIN, SILVER, by fusing, with incrustation of the charcoal (comp. 16); COPPER by the green coloration of the outer flame. Further conclusions may be formed when the substance is a single metal nearly pure; thus, for instance, GOLD fuses without incrustation; PLATINUM,

IRON, MANGANESE, NICKEL, and COBALT, do not fuse in the blowpipe flame.

3. HEAT A SAMPLE OF THE SUBSTANCE BEFORE THE BLOW- 24
PIPE IN A GLASS TUBE SEALED AT ONE END.

a. NO SUBLIMATE IS FORMED IN THE COLDER PART OF THE TUBE: absence of mercury.

b. A SUBLIMATE IS FORMED: presence of MERCURY, CADMIUM or ARSENIC. The sublimate of mercury, which consists of small globules, cannot be confounded with that of cadmium or arsenic.

After the termination of the preliminary examination, proceed to the solution of the substance, as directed § 181 (42).

§ 178.

B. THE SUBSTANCE UNDER EXAMINATION IS A FLUID.

1. EVAPORATE A SMALL PORTION OF THE FLUID in a plati- 25
num capsule, or in a small porcelain crucible, to ascertain whether it actually contains any matter in solution; if a residue remains, examine this as directed § 176.

2. TEST WITH LITMUS PAPER (blue and red).

a. THE FLUID REDDENS BLUE LITMUS PAPER. This re- 26
action may be caused by a free acid or an acid salt, as well as by normal salts of the heavy metals,* soluble in water. To distinguish between these two cases, pour a small quantity of the fluid into a watch glass, and dip into it a small glass rod, after moistening the extreme point of the latter with dilute solution of sodium carbonate; if the fluid remains clear, or if the precipitate which may form at first redissolves upon stirring the liquid, this proves the presence of a free acid or of an acid salt; but if the fluid becomes turbid and remains so, this generally denotes the presence of a soluble salt of a heavy metal.

b. REDDENED LITMUS PAPER TURNS BLUE; this indicates 27
the presence of an alkali or alkali-earth metal, usually in the state of hydroxide, sulphide or carbonate.

3. SMELL THE FLUID, or, should this fail to give satisfac- 28
tory results, DISTIL, to ascertain whether the simple sol-

* *I.e.*, of other than an alkali or alkali-earth metal.

vent present is water, alcohol, ether, etc. If you find it is not water, evaporate the solution to dryness and treat the residue as directed § 176.

4. If the solution is aqueous, and manifests an acid re- 29
action, DILUTE A PORTION OF IT LARGELY WITH WATER. Should this impart a milky appearance to it, the presence of ANTIMONY or BISMUTH (or possibly also of tin) may be inferred. Comp. § 121, 9, and § 131, 4.

On completing the Preliminary Examination of a Fluid 30
the operator may proceed to its Actual Analysis. If the solution is aqueous and *reacts neutral*, only bodies which are soluble in water can be present; if, on the contrary, it has an *acid reaction*, which may be due to the presence of *a free acid*, it can no longer be considered simply aqueous, and the analysis must be conducted with regard to the possible presence of substances insoluble in water but soluble in acids.

These circumstances being properly considered, the analyst passes over to § 182; solutions having an alkaline reaction are also examined according to § 182.

II. SOLUTION OF BODIES, OR CLASSIFICATION OF SUBSTANCES ACCORDING TO THEIR DEPORTMENT WITH CERTAIN SOLVENTS.

☞ *Consult the remarks in the Third Section, page* 416.

§ 179.

Water and acids (hydrochloric acid, nitric acid, aqua 31
regia) are the solvents used to classify simple or compound substances, and to isolate the component parts of mixtures. We divide the various substances into three classes, according to their respective deportment with these solvents.

First class.—SUBSTANCES SOLUBLE IN WATER.

Second class.—SUBSTANCES INSOLUBLE OR SPARINGLY SOLUBLE IN WATER, BUT SOLUBLE IN HYDROCHLORIC ACID, NITRIC ACID, OR AQUA REGIA.

Third class.—SUBSTANCES INSOLUBLE OR SPARINGLY SOLUBLE IN WATER AS WELL AS IN HYDROCHLORIC ACID, NITRIC ACID, OR AQUA REGIA.

The solution of ALLOYS being more appropriately effected in a different manner from that pursued with other bodies, I shall give a special method for these substances (see § 181).

The process of solution is conducted in the following manner:

A. THE SUBSTANCE UNDER EXAMINATION IS NEITHER A METAL NOR AN ALLOY.

§ 180.

1. Put about a gramme of the finely pulverized sub- 32
stance into a small flask or a test-tube, add from ten to twelve times the amount of distilled water, and heat to boiling over a spirit or gas lamp.

a. THE SUBSTANCE DISSOLVES COMPLETELY. In that 33
case it belongs to the first class: regard must be had to what has been stated in the preliminary examination (**30**) with respect to reaction with test-papers. Treat the solution as directed § 182, **46.**

b. AN INSOLUBLE RESIDUE REMAINS EVEN AFTER PRO- 34
TRACTED BOILING. Let the residue subside, and filter the fluid off, if practicable, in such a manner as to retain the residue in the test-tube; evaporate a few drops of the clear filtrate on platinum foil; if nothing remains, the substance is completely insoluble in water; in which case proceed as directed **35.** But if a residue remains, the substance is at least partly soluble; in which case boil again with water, filter, add the filtrate to the first solution, and treat the fluid as directed § 182. Wash the residue with water, and proceed as directed **35.**

2. Treat a small portion of the residue which has been 35
boiled with water (**34**) with dilute hydrochloric acid. If it does not dissolve, heat to boiling, and if this fails to effect complete solution, decant the fluid into another test-tube, boil the residue with concentrated hydrochloric acid, and, if it dissolves, add the solution to the fluid in the other test-tube.

The reactions which may manifest themselves in this

operation, and which ought to be carefully observed, are (α) Effervescence, which indicates the presence of carbonic acid or hydrosulphuric acid; (β) Evolution of chlorine, which indicates the presence of metallic dioxides, chromates, etc.; (γ) Emission of the odor of hydrocyanic acid, which indicates the presence of insoluble cyanides. The analysis of the latter bodies being effected in a somewhat different manner, a special paragraph will be devoted to them (see § 197).

a. THE RESIDUE IS COMPLETELY DISSOLVED BY THE HYDROCHLORIC ACID (except perhaps that sulphur separates, which may be known by its color and light specific gravity, and may, after boiling some time longer, be removed by filtration; or that gelatinous silicic acid separates). Proceed, according as directed § 183, after filtration if necessary. The body belongs to the second class. To make quite sure of the actual nature of the sulphur or silicic acid filtered off, examine these residuary matters as directed § 196. **36**

b. THERE IS STILL A RESIDUE LEFT. In that case put aside the test-tube containing the specimen which has been boiled with the hydrochloric acid, and try to dissolve another sample of the substance insoluble in water, or already extracted with water, by boiling with nitric acid, and subsequent addition of water. Evolution of gaseous oxides of nitrogen, by the action of the nitric acid, shows that a process of oxidation is taking place. **37**

α. The sample is completely dissolved, or leaves no other residue but sulphur or gelatinous silicic acid. In this case also the body belongs to the second class. Use this solution to test further for metals as directed § 182, **46**, and for the rest proceed as in **36**. **38**

β. There is still a residue left. Pass on to **40**. **39**

3. If the residue insoluble in water will not entirely dissolve in hydrochloric acid nor in nitric acid, try to effect complete solution of it by means of nitro-hydrochloric acid. To this end mix the contents of the tube treated with nitric acid with the contents of the tube treated with concentrated hydrochloric acid; heat the mixture to boil- **40**

ing, and should this fail to effect complete solution, decant the clear fluid off from the undissolved residue, boil the latter for some time with concentrated nitro-hydrochloric acid, and add the decanted solution in dilute aqua regia as well as the solution in dilute hydrochloric acid, decanted in **35**. Heat the entire mixture once more to boiling, and observe whether complete solution has now been effected, or whether the action of the concentrated nitro-hydrochloric acid has still left a residue. In the *latter* case filter the solution—if necessary after addition of some water*—wash the residue with boiling water, and proceed with the filtrate, and the washings added to it, as directed § 183. In the *former* case proceed with the clear solution in the same way.†

4. If boiling nitro-hydrochloric acid has left an undis- **41** solved residue, wash it thoroughly with water, and then proceed as directed § 196.

B. The Substance under Examination is a Metal or an Alloy.

§ 181.

The metals are best classed according to their behavior **42** with nitric acid, as follows:

I. Metals which are not attacked by nitric acid: gold, platinum.

II. Metals which are oxidized by nitric acid, but whose oxides do not dissolve in an excess of the acid or in water: antimony, tin.

III. Metals which are oxidized by nitric acid and converted into nitrates which dissolve in an excess of the acid or in water: all the other metals.

Pour nitric acid of 1.20 sp. gr. over a small portion of the substance, and apply heat.

* If the fluid turns turbid upon addition of water, this indicates the presence of bismuth or antimony; the turbidity will disappear again upon addition of hydrochloric acid.

† Where the acid solution on cooling deposits acicular crystals, the latter generally consist of lead chloride; it is in that case often advisable to decant the fluid off the crystals, and to examine the fluid and crystals separately. Where on boiling with aqua regia metastannic chloride has been formed from stannic hydroxide, the washing water, dissolving this, becomes turbid on dropping into the strongly acid fluid which has run off first. In that case receive the washing water in a separate vessel, and treat the two solutions separately with hydrosulphuric acid, as directed in § 183, but filter afterwards through the same filter.

1. COMPLETE SOLUTION TAKES PLACE, EITHER AT ONCE OR UPON ADDITION OF WATER; this proves the absence of platinum,* gold, antimony,† and tin. Proceed as directed § 182, III. (53). 43

2. A RESIDUE IS LEFT.

a. A metallic residue. Filter, and treat the filtrate as directed § 182, III. (53), after having seen, in the first place, whether anything has really been dissolved. Wash the residue thoroughly, dissolve in nitro-hydrochloric acid, and test the solution for GOLD and PLATINUM, according to § 128. 44

b. A white pulverulent residue: indicates ANTIMONY and TIN. Treat another portion with aqua regia. If complete solution takes place, evaporate off the greater part of the free acid, dilute with water, and treat the solution as directed in § 183. A residue left by aqua regia indicates SILVER or LEAD, and is examined according to § 182 (47). 45

Or filter, ascertain whether anything has been dissolved, then treat the filtrate as directed § 182, III. (53). Wash the residue thoroughly, then test for ANTIMONIOUS OXIDE, STANNIC OXIDE, and ARSENIC ACID, according to § 184, 5. (Part, at least, of the arsenic acid is always found in this precipitate, combined with antimony and tin.)

III. ACTUAL ANALYSIS.

A. SUBSTANCES SOLUBLE IN WATER, AND ALSO SUCH AS ARE INSOLUBLE IN WATER, BUT DISSOLVE IN HYDROCHLORIC ACID, NITRIC ACID, OR NITRO-HYDROCHLORIC ACID.

Detection of Metals.‡

§ 182.

(*Treatment with Hydrochloric Acid: Detection of Silver, Mercury in mercurous compounds* [*Lead*].)

☞ *The operator should carefully study the Notes in Section III. before going further, and should review them frequently until familiar with their contents: see pp.* 419 *and* 427.

* Alloys of silver and platinum, with the latter metal present in small proportion only, dissolve in nitric acid.

† Very minute traces of antimony, however, are often completely dissolved by nitric acid.

‡ Regard is here had also to the presence of those salts of the alkali-earth metals which dissolve in H Cl and separate again from that solution unaltered upon neutralization of the acid by NH_4OH; viz.: phosphates, borates, etc.

I. The Solution is in Water.

Mix the portion intended for the detection of the 46
metals with some hydrochloric acid.

1. The solution had an acid or neutral reaction previously to the addition of the hydrochloric acid.

a. No precipitate is formed: this indicates the absence of silver and (mercurous) mercury. Pass on to § 183.

b. A precipitate is formed. Add more H Cl, drop by drop, until the precipitate ceases to increase; then add about six or eight drops more of H Cl, shake the mixture, and filter.

The precipitate produced by H Cl may consist of silver chloride, mercurous chloride, lead chloride, a basic salt of antimony, bismuth oxychloride, metastannic chloride, possibly also benzoic acid. The basic salt of antimony and the bismuth oxychloride, however, redissolve in the excess of H Cl; consequently, if the instructions given have been strictly followed, the precipitate collected upon the filter can consist only of silver chloride, mercurous chloride, or lead chloride (possibly also of the very rare metastannic chloride and benzoic acid, which, however, are disregarded *here*).

Wash the precipitate collected upon the filter twice with cold water, add the washings to the filtrate, and examine the solution as directed § 183, even though the addition of the washings to the acid filtrate should produce turbidity in the fluid (which indicates the presence of antimony or bismuth, or possibly also of metastannic chloride).

Treat the twice-washed precipitate on the filter as 47
follows:

a. Pour hot water over it upon the filter, and test the fluid running off with H_2S and with H_2SO_4 for lead. (The non-formation of a precipitate simply proves that the precipitate produced by H Cl contains no Pb, and does not by any means establish the total absence of this metal, as H Cl fails to precipitate Pb from dilute solutions.) If

the H Cl precipitate contains Pb Cl_2, wash it several times with hot water to dissolve out the lead.

β. If there is a residue remaining on the filter, treat it with ammonia. If this changes its color to black or gray, it is a proof of the presence of MERCUROUS OXIDE.

γ. Add to the ammoniacal fluid running off in *β*, H N O_3 to strongly acid reaction. The formation of a white, curdy precipitate indicates the presence of SILVER.* (If the precipitate still contained lead, the ammoniacal solution generally appears turbid, owing to the separation of a basic lead salt. This, however, does not interfere with the testing for silver, since the basic lead salt redissolves upon the addition of H N O_3.)

2. THE ORIGINAL AQUEOUS SOLUTION HAD AN ALKALINE REACTION. 48

a. THE ADDITION OF HYDROCHLORIC ACID TO STRONGLY ACID REACTION FAILS TO PRODUCE EVOLUTION OF GAS OR A PRECIPITATE, OR THE PRECIPITATE WHICH FORMS AT FIRST REDISSOLVES UPON FURTHER ADDITION OF HYDROCHLORIC ACID: pass on to § 183.

b. THE ADDITION OF HYDROCHLORIC ACID PRODUCES A PRECIPITATE WHICH DOES NOT REDISSOLVE IN AN EXCESS OF THE PRECIPITANT, EVEN UPON BOILING.

α. The formation of the precipitate is attended neither with evolution of hydrosulphuric nor of hydrocyanic acid. Filter, and treat the filtrate as directed § 183. 49

aa. THE PRECIPITATE IS WHITE. It may, in that case, consist of a salt of lead or silver, insoluble, or difficultly soluble in H_2O and H Cl (LEAD CHLORIDE, LEAD SULPHATE, SILVER CHLORIDE, etc.), or it may be SILICIC ACID. Test it for the bases and acids of these compounds as directed § 196, bearing in mind that the lead chloride or silver chloride which may be found may possibly have been formed in the process.

bb. THE PRECIPITATE IS YELLOW OR ORANGE. In that case it may consist of ARSENIOUS SULPHIDE,

* If the quantity of silver is only very small, its presence is indicated by opalescence of the fluid.

and if the fluid from which it has separated was not boiled long, or only with very dilute H Cl, also of ANTIMONIOUS SULPHIDE or STANNIC SULPHIDE, which substances were originally dissolved in ammonia, potassa, soda, sodium phosphate, or some other alkaline fluid, with the exception of alkali sulphides and cyanides. Examine the precipitate, which may also contain SILICIC ACID, as directed **40.**

*β. The formation of the precipitate is attended with evolution of hydrosulphuric acid, but not of hydrocyanic acid.** **50**

aa. THE PRECIPITATE IS OF A PURE WHITE COLOR, AND CONSISTS OF SEPARATED SULPHUR. In that case a POLYSULPHIDE OF AN ALKALI METAL is generally present. The presence of such a body may be detected also by the yellow or brownish-yellow color of the alkaline solution, and the odor of hydrogen disulphide (H_2S_2), which accompanies that of H_2S on the addition of an acid. Boil, filter, and treat the filtrate as directed § 187, the precipitate as directed § 196.

bb. THE PRECIPITATE IS COLORED. In that case you may conclude that a SULPHUR SALT is present.† The precipitate may accordingly consist of AURIC SULPHIDE, PLATINIC SULPHIDE, STANNIC SULPHIDE, ARSENIOUS SULPHIDE, or ANTIMONIOUS SULPHIDE. It might, however, consist also of MERCURIC SULPHIDE or of CUPRIC SULPHIDE or NICKEL SULPHIDE, or contain these substances, as the former will dissolve readily in K_2S, and in small quantities in $(NH_4)_2S$, and the latter are slightly soluble in $(NH_4)_2S$. Filter and treat the filtrate as directed § 187, the precipitate as directed **40.**

γ. The formation of the precipitate is attended with evolution of hydrocyanic acid, with or without simultaneous disengagement of hydrosulphuric acid. This indicates the presence of an ALKALI CYANIDE, and if **51**

* Should the odor of the evolved gas leave any doubt regarding the actual presence or absence of H C N, add some potassium chromate to a portion of the fluid, previously to the addition of the H Cl.

† See p. 51.

the evolution of H C N is attended with that of H_2S, also of an ALKALI SULPHIDE. In that case the precipitate may, besides the compounds enumerated in α and β, contain many other substances (*e.g.*, nickel cyanide, silver cyanide, etc.). Boil, with further addition of H Cl or H N O_3, until the whole of the H C N is expelled, and treat the solution, or, if an undissolved residue has been left, the filtrate, as directed § 183; and the residue (if any) according to § 196 or § 197.

c. THE ADDITION OF HYDROCHLORIC ACID FAILS TO PRODUCE A PERMANENT PRECIPITATE, BUT CAUSES EVOLUTION OF GAS. **52**

α. The escaping gas smells of hydrosulphuric acid: this indicates a SIMPLE ALKALI SULPHIDE, or A SULPHUR SALT OF AN ALKALI or ALKALI-EARTH METAL. Proceed as directed § 187.

β. The escaping gas is inodorous: in that case it is CARBON DIOXIDE, which was combined with an alkali. Pass on to § 183.

γ. The escaping gas smells of hydrocyanic acid: (no matter whether H_2S or CO_2 is evolved at the same time or not). This indicates an ALKALI CYANIDE. Boil until the whole of the H C N is expelled, then pass on to § 183.

II. THE SOLUTION IS IN HYDROCHLORIC ACID OR IN NITRO-HYDROCHLORIC ACID.

Proceed as directed § 183.

III. THE SOLUTION IS IN NITRIC ACID.

Dilute a small portion; should this produce turbidity or a precipitate (indicative of Bi), add H N O_3 until the fluid is clear again, then H Cl. **53**

1. NO PRECIPITATE IS FORMED. Absence of silver and (mercurous) mercury. Treat the principal solution as directed § 183.

2. A PRECIPITATE IS FORMED. Treat a larger portion of the H N O_3 solution in the same way, filter, and examine the precipitate as directed **47**, the filtrate as directed § 183.

§ 183.

☞ *Do not fail to consult page* 420 *and also page* 429.

(*Treatment with Hydrosulphuric Acid. Precipitation of the Metals of Group V., 2d Division, and of Group VI.*)

ADD TO A *small* PORTION OF THE CLEAR ACID SOLUTION HYDROSULPHURIC ACID WATER, UNTIL THE ODOR OF HYDROSULPHURIC ACID IS DISTINCTLY PERCEPTIBLE AFTER SHAKING THE MIXTURE, AND WARM GENTLY.

1. NO PRECIPITATE IS FORMED, even after the lapse of some time. Pass on to § 187, for lead, bismuth, cadmium, copper, mercury, gold, platinum, antimony, tin, and arsenic,* are not present;† the absence of tetrad iron and of chromates is also indicated by this negative reaction. **54**

2. A PRECIPITATE IS FORMED.

a. The precipitate is of a pure white color, light, and finely pulverulent, and does not redissolve on addition of H Cl. It consists of separated sulphur, and indicates the presence of IRON AS A FERRIC SALT.‡ None of the other metals enumerated in **54** can be present. Treat the principal solution as directed § 187. **55**

b. The precipitate is colored.

Add to the larger proportion of the acid or acidified solution, best in a small flask, H_2S water in excess, *i.e.*, until the fluid smells distinctly of it after shaking, and the precipitate ceases to increase upon continued addition of the reagent; apply a gentle heat, shake vigorously for some time, filter, keep the filtrate (which contains the metals present of Groups I.–IV.) for further examination accord- **56**

* Where the preliminary examination has led you to suspect the presence of As O $(OH)_3$, you must endeavor to obtain the most conclusive evidence of the absence of this acid; this may be done by allowing the fluid to stand for some time at a gentle heat (about 70°), or by heating it with sulphurous acid previous to the addition of the H_2S. (Compare § 133, 3.)

† In solutions containing much free acid, the precipitates are frequently formed only after dilution with water.

‡ Sulphur will precipitate also if sulphurous acid, or iodic acid, or bromic acid is present (which substances are not included in our analytical course), and also if chromic acid, or chloric acid, or free chlorine is present. In presence of chromic acid the separation of the sulphur is attended with reduction of the acid to chromic oxide, in consequence of which the reddish-yellow color of the solution changes to green. (Compare § 138.) The white sulphur suspended in the green solution looks at first like a green precipitate, which frequently tends to mislead beginners.

ing to § 187, and *thoroughly* wash * the precipitate, which contains the sulphides of the metals present of Groups V. and VI.

In many cases, and more particularly where there is any reason to suspect the presence of arsenic, it will be found more convenient to transmit H_2S gas through the solution DILUTED WITH WATER, instead of adding H_2S water. When arsenic is suspected it is also well to keep the fluid at about 70° C. during the transmission of the gas.

If the precipitate is yellow, it consists principally **57** of arsenious sulphide, stannic sulphide or cadmium sulphide; if orange colored, this indicates antimonious sulphide; if brown or black, one at least of the following metals is present: lead, bismuth, copper, mercury as mercuric salt, gold, platinum, dyad tin. However, as a yellow precipitate may contain small particles of an orange-colored, a brown, or even a black precipitate, and yet its color not be very perceptibly altered thereby, it will always prove the safest way to assume the presence of all the metals named in **54** in any precipitate produced by H_2S, and to proceed as the next paragraph (§ 184) directs.

§ 184.

☞ *Consult the notes on pages 420 and 429.*

(*Treatment of the Precipitate produced by Hydrosulphuric Acid with Ammonium Sulphide; Separation of the 2d Division of Group V. from Group VI.*)

INTRODUCE A SMALL PORTION OF THE THOROUGHLY WASHED **58** PRECIPITATE PRODUCED BY HYDROSULPHURIC ACID IN THE ACIDIFIED SOLUTION INTO A TEST-TUBE, † ADD A LITTLE WATER, AND FROM TEN TO TWENTY DROPS OF YELLOW AMMONIUM SULPHIDE

* Compare § 7.

† If there is a somewhat large precipitate, this may be readily effected by means of a small spatula of platinum or horn; but if you have only a very trifling precipitate, make a hole in the bottom of the filter, and rinse the precipitate into the test-tube by means of the washing-bottle, wait until the precipitate has subsided, and then decant the water.

AND EXPOSE THE MIXTURE FOR A SHORT TIME TO A GENTLE HEAT.

1. THE PRECIPITATE DISSOLVES COMPLETELY IN AMMONIUM SULPHIDE; absence of the metals of Group V.—cadmium, lead, bismuth, copper,* mercury. Treat the remainder of the precipitate, of which you have digested a portion with $(NH_4)_2S_x$, as directed § 185. If the precipitate produced by H_2S was so trifling that you have used the whole of it in treating with $(NH_4)_2S_x$, precipitate the solution obtained in that process by addition of HCl, filter, wash the precipitate, and treat it as directed § 185. 59

2. THE PRECIPITATE IS NOT REDISSOLVED, OR AT LEAST NOT COMPLETELY, even on heating with more ammonium sulphide: presence of metals of Group V. Dilute with 4 or 5 parts of water, filter, and mix the filtrate with HCl in slight excess. 60

a. A pure white turbidity is occasioned, owing to the separation of sulphur. Absence of the metals of Group VI.—gold, platinum, tin, antimony, and arsenic.† Treat the rest of the precipitate, of which you have digested a portion with $(NH_4)_2S_x$, according to § 186.

b. A colored precipitate is formed: presence of metals of Group VI., and of Group V. Treat the entire precipitate produced by H_2S as you have treated the portion, *i.e.* digest it with yellow ammonium sulphide, let subside, pour the supernatant liquid on a filter, digest the residue in the tube once more with yellow ammonium sulphide, and filter. Wash the residue‡ 61

* COPPER, if not already revealed by the preliminary examination, should be tested for, at this stage of the analysis, in a portion of the original solution by means of a clean iron rod (see § 120); because it may be dissolved to a considerable extent (as a cuprous sulphur salt), by concentrated and very yellow ammonium sulphide, especially in presence of Sn, Sb, and As.

† That this inference becomes uncertain if the precipitate produced by H_2S, instead of being digested with a small quantity of $(NH_4)_2S_x$, has been treated with a large quantity of that reagent, is self-evident; for the large quantity of sulphur which separates in that case will of course completely conceal any slight traces of As_2S_3 or SnS_2 which may have been thrown down. Compare also notes to § 103 and § 184 in the Third Section.

‡ If the residue suspended in the fluid containing $(NH_4)_2S_x$, and insoluble therein, subsides readily, it is not transferred to the filter, but washed in the tube by decantation. But if its subsidence proceeds slowly and with difficulty, it is transferred to the filter, and washed there; a hole is then made in the bottom of the filter, and the residue rinsed into a small porcelain basin by means of a washing-bottle; the application of a gentle heat will now materially aid the subsidence of the residue, and the supernatant water may then be decanted. The sulphides are occasionally suspended in the fluid in a state of such minute division that the fluid cannot be filtered off clear. In cases of the kind some NH_4Cl should be added to the fluid, and it should be allowed to settle at a gentle heat for some time before being filtered.

(containing the sulphides of Group V.), and treat it afterwards as directed § 186. Dilute the filtrate (which contains the metals of Group VI. in the form of sulphur salts), add H Cl to distinctly acid reaction, heat gently, filter off the precipitate, which contains the sulphides of the metals of Group VI. mixed with sulphur, wash thoroughly, and proceed as directed in the next paragraph (§ 185).

§ 185.

☞ *Consult the notes in the Third Section: page* 431.

(*Detection of the Metals of Group VI.: Arsenic, Antimony, Tin, Gold, Platinum.*)

If the precipitate consisting of the sulphides of Group VI. has a PURE YELLOW COLOR, this indicates principally arsenic and tetrad tin; if in the proved absence of copper it is distinctly ORANGE-YELLOW, antimony is sure to be present; if it is BROWN or BLACK, this denotes the presence of dyad tin, platinum, or gold. **62**

Beyond these general indications the color of the precipitate affords no safe guidance. It is therefore always advisable to test a yellow precipitate also for antimony, gold, and platinum, since minute quantities of the sulphides of these metals are completely hidden by a large quantity of stannic sulphide, or arsenious sulphide. Proceed accordingly as follows:

Heat a little of the precipitate on the lid of a porcelain crucible, or on a piece of porcelain or glass.*

1. *Complete volatilization ensues:* probable presence of ARSENIC, absence of the other metals of Group VI. Confirm by reduction of a portion of the precipitate with K C N and $Na_2 Co_3$ (§ 132, 13).† Whether that metal was present in the arsenious or in the arsenic form may be ascertained by the methods described § 134, 9. **63**

2. *A fixed residue is left.* In that case all the metals of **64**

* That this preliminary examination may be omitted if the precipitate has any other color than yellow, and that it can give a decisive result only if the precipitate has been thoroughly washed, are self-evident.

† In cases where the precipitate contains much free S, dissolve the $As_2 S_3$ which may be present, by digestion in $(N H_4)_2 C O_3$, filter, evaporate the solution with addition of a small quantity of $Na_2 C O_3$, to dryness, and heat the residue with $Na_2 C O_3$.

Group VI. must be sought for. In *absence of copper*,* dry the remainder of the precipitate thoroughly upon the filter, triturate it with about 1 part of dry $Na_2 C O_3$ and 1 part of $Na N O_3$, and transfer the mixture in small portions at a time to a porcelain crucible, in which you have previously heated 2 parts of $Na N O_3$ to fusion.† As soon as complete oxidation is effected, pour the mass on to a piece of porcelain. After cooling soak the fused mass ‡ (the portion still sticking to the inside of the crucible as well as the portion poured out on the porcelain) in cold water, filter from the insoluble residue—which will remain if the mass contained antimony, tin, gold, or platinum—and wash thoroughly with a mixture of about equal parts of water and alcohol. (The alcohol is added to prevent the solution of the $Na Sb O_3$. The washings are not added to the filtrate.) The filtrate and the residue are now examined as follows:

a. EXAMINATION OF THE FILTRATE FOR ARSENIC (which must be present in it in the form of $Na_3 As O_4$). Add nitric acid to the fluid to distinct acid reaction,§ heat to expel $C O_2$ and $N_2 O_4$, then divide the fluid into two portions. Add to the one portion some $Ag N O_3$ (not too little), filter (in case Ag Cl ‖ or $Ag N O_3$ should have separated), pour upon the filtrate, along the side of the tube held slanting, a layer of dilute solution of ammonia—2 parts of water to 1 part of solution of ammonia—and allow to stand some time without 65

* [If *copper be present* in the original substance it may also be contained in this precipitate in such quantities as to render the detection of antimony uncertain. In such a case it is best to treat the remainder of the precipitate at a boiling heat with sodium sulphide, which will dissolve only the sulphides of Group VI. Then filter from the cupric sulphide, dilute the solution, precipitate again the sulphides of Group VI. by addition of H Cl in slight excess, warm, filter, wash thoroughly, and proceed as directed, 64.—EDITOR.]

† Should the amount of the precipitate be so minute that this operation cannot be conveniently performed, cut the filter, with the dried precipitate adhering to it, into small pieces, triturate these with some $Na_2 C O_3$ and $Na N O_3$, and project both the powder and the paper into the fusing $Na N O_3$. It is *preferable*, however, in such cases, to procure, if practicable, a larger amount of the precipitate, as otherwise there will be but little hope of effecting the positive detection of all the metals of Group VI.

‡ Supposing all the metallic sulphides of the sixth group to have been present, the fused mass would consist of antimonate and arsenate of sodium, stannic oxide, metallic gold and platinum, sulphate, carbonate, nitrate, and some nitrite of sodium. Compare also § 134, 1. When gold and tin are present together the fused mass often has a peculiar light-red color.

§ In some cases where a somewhat large proportion of $Na_2 C O_3$ has been used, or a very strong heat applied, a trifling precipitate (stannic acid) may separate upon the acidification of the filtrate with $H N O_3$. This may be filtered off, and then treated in the same manner as the undissolved residue.

‖ Ag Cl will separate if the reagents were not perfectly pure, or the precipitate has not been thoroughly washed.

shaking. The formation of a reddish-brown precipitate or cloud between the two layers (seen most readily by reflected light), denotes the presence of ARSENIC.

If the arsenic is present in some quantity, and the free nitric acid of the solution is exactly saturated with ammonia, the fluid being stirred during this process, the precipitate of Ag_3AsO_4, which forms imparts a brownish-red tint to the entire fluid.

Add to the other portion of the acidified solution, **66** first, NH_4OH, then magnesium mixture;* and rub the interior walls of the vessel with a glass rod. A crystalline precipitate of $NH_4MgAsO_4 + 6H_2O$, which often forms only after long standing, and is deposited more particularly on the sides of the vessel, shows the presence of arsenic. By way of confirmation the precipitate may be washed with water containing NH_4OH, dissolved in dilute HCl, and the solution precipitated by H_2S, with the aid of a gentle heat, or the arsenic may be reduced to the metallic state (compare § 132 and § 133). Whether the arsenic was present in the arsenious or arsenic form, may be ascertained by the methods described § 134, 9.

b. EXAMINATION OF THE RESIDUE FOR ANTIMONY, TIN, **67** GOLD, PLATINUM. (As the antimony, if present in the residue, must exist as white pulverulent sodium antimonate, the tin as white stannic oxide, the gold and platinum in the metallic state, the appearance of the residue is in itself indicative of its nature. But it must be noted that on account of the solubility of cuprous sulphide in ammonium sulphide, cupric oxide may also be present in this residue [unless copper has been separated by Na_2S, as directed in the first note, p. 320.—EDITOR]). Transfer the precipitate to the lid of a platinum crucible, or to a platinum capsule, heat with HCl, add a little water, and throw in a small compact lump of pure zinc (more particularly free from lead), no matter whether the precipitate has completely dissolved or not in the HCl. This operation leaves the gold and platinum in the same state in

* See note to p. 212.

which the fused mass contained them, viz., in the metallic state, to which the tin and antimony are now likewise reduced by the action of the zinc. The ANTIMONY reveals its presence at once, or after a short time, by blackening the platinum. As soon as the disengagement of hydrogen has nearly stopped, take out the lump of zinc, remove the solution of $Zn Cl_2$ by cautious decantation, warm the metals with H Cl, and test the solution—which, if TIN is present, must contain stannous chloride, with mercuric chloride (§ 129, 8). In what state of quantivalence tin or antimony were originally present may be ascertained according to § 134, 7 and 8.

After removing the tin by repeated boiling with 68
H Cl, and all the H Cl by thoroughly washing with water, examine the insoluble residue (if one is left) as follows: Heat it in the platinum lid with some water, with addition of a few grains of tartaric acid, then add some nitric acid, and heat gently. If the residue dissolves completely, no gold or platinum is present; if a residue is left undissolved, you must test it for these metals. For this purpose remove the acid solution (which may be tested again for ANTIMONY with H_2S) by decantation and washing, transfer the residue to a porcelain dish, heat with a little aqua regia, evaporate the solution to a small volume and test for GOLD and PLATINUM as directed § 128.

§ 186.

☞ *Consult the notes on pages 420 and 431.*

(*Detection of the Metals of Group V., 2d Division:—Lead, Bismuth, Copper, Cadmium, Mercury.*)

THOROUGHLY WASH THE PRECIPITATE WHICH HAS NOT BEEN 69
DISSOLVED BY AMMONIUM SULPHIDE, AND BOIL WITH DILUTE NITRIC ACID. This operation is performed best in a small porcelain dish: the boiling mass must be constantly stirred with a glass rod. A great excess of acid must be avoided.

1. THE PRECIPITATE DISSOLVES, AND THERE REMAINS FLOAT- 70
ING IN THE FLUID ONLY THE SEPARATED LIGHT FLOCCULENT

AND YELLOW SULPHUR: this indicates the absence of mercury. CADMIUM, COPPER, LEAD and BISMUTH may be present. Filter from the separated sulphur, and treat the filtrate as follows (should there be too much HNO_3 present, the greater part of this must first be driven off by evaporation): Add to a portion of the filtrate dilute H_2SO_4 in moderate quantity, heat gently, and allow to stand some time.

a. NO PRECIPITATE FORMS: absence of lead. Mix the remainder of the filtrate with NH_4OH in excess, and gently heat. **71**

α. No precipitate is formed: absence of bismuth. If the liquid is blue, COPPER is present; very minute traces of copper, however, might be overlooked if the color of the ammoniated fluid alone were consulted. To be quite safe, and also to test for cadmium, evaporate the ammoniated solution nearly to dryness, add a little acetic acid, and, if necessary, some water, and **72**

aa. Test a small portion of the fluid for copper with $K_4Fe(CN)_6$. A reddish-brown precipitate or a light brownish-red turbidity indicates COPPER (in the latter case only to a very trifling amount). **73**

bb. To the remainder, if copper is absent, add H_2S. A yellow precipitate indicates CADMIUM. If copper is present it is most conveniently removed in the form of cuprous sulphocyanate by means of sulphurous acid and KCNS, and the filtrate, after being evaporated to drive off excess of SO_2, is tested for cadmium with H_2S. Or both metals may be precipitated by H_2S, and then separated by KCN (in which case the sulphides must have been recently precipitated) or by boiling dilute H_2SO_4 (§ 123). **74**

β. A precipitate is formed. BISMUTH is present. Filter and test the filtrate for copper and cadmium as directed **72**. To test the washed precipitate more fully for bismuth, slightly dry the filter containing it between blotting paper, remove the still moist precipitate with a platinum spatula, dissolve on a watch glass in the *least possible quantity* of HCl, **75**

and then add water. The appearance of a milky turbidity confirms the presence of bismuth.

b. A PRECIPITATE IS FORMED. Presence of LEAD. **76** Mix the whole of the HNO_3 solution in a porcelain dish with a sufficient quantity of dilute H_2SO_4, evaporate on the water bath until the HNO_3 is expelled, dilute the residue with some water containing H_2SO_4, filter off at once the $PbSO_4$ left undissolved, and test the filtrate for bismuth, copper and cadmium, as directed **71.*** Test the precipitate, after washing, by one of the methods in § 123.

2. THE PRECIPITATE OF THE SULPHIDES DOES NOT COMPLETELY DISSOLVE IN THE BOILING NITRIC ACID, BUT LEAVES A RESIDUE, BESIDES THE SULPHUR THAT FLOATS IN THE FLUID. **77** Probable presence of MERCURY (as mercuric salt) (which may be pronounced almost certain if the precipitate is heavy and black). Allow the precipitate to subside, filter off the fluid, which is still to be tested for CADMIUM, COPPER, LEAD and BISMUTH; mix a small portion of the filtrate with a large amount of solution of H_2S, and should a precipitate form or a coloration become visible, treat the remainder of the filtrate according to **70.**

Wash the residue (which may, besides HgS, also contain $PbSO_4$, formed by the action of HNO_3 upon PbS, and also SnO_2, and possibly Au_2S_3 and PtS_2, as the separation of the sulphides of tin, gold and platinum from the sulphides of the metals of the fifth group is often incomplete), and examine one-half of it for mercury,† by dissolving it in some HCl, with addition of a very small portion of potassium chlorate, and testing the solution with copper or stannous chloride (§ 119); fuse the other half with KCN and Na_2CO_3, and treat the fused mass with water. If metallic grains remain, or if a metallic powder is left undissolved, wash this residue, heat with HNO_3, and test the solution obtained with H_2SO_4 for lead. Wash the residue which the HNO_3 may leave undissolved, and extract from it any metastannic acid which it may contain,

* For another method of separating Cd, Cu, Pb, and Bi, see the Third Section, page 481.

† If you have an aqueous solution, or a solution in very dilute HCl, the mercury found was present in the original substance in the mercuric form; but if the solution has been prepared by boiling with concentrated HCl, or by heating with HNO_3 or aqua regia, the mercury may have been originally present in the mercurous form.

according to § 130, 1, as metastannic chloride. Should a metallic powder be left undissolved in the process, heat it with aqua regia, and test the solution for gold and platinum as directed § 128.

§ 187.

☞ *Compare the notes on pp.* 420 *and* 432.

(*Precipitation with Ammonium Sulphide, Separation and Detection of the Metals of Groups III. and IV.: Aluminium, Chromium; Zinc, Manganese, Nickel, Cobalt, Iron; and also of those Salts of the Alkali-Earth Metals which are precipitated by Ammonia from their Solutions in Hydrochloric Acid: Phosphates, Borates, Oxalates, Silicates, and Fluorides.*)

PUT A *small portion* OF THE FLUID IN WHICH HYDROSULPHURIC ACID HAS FAILED TO PRODUCE A PRECIPITATE (**54**), OR OF THE FLUID WHICH HAS BEEN FILTERED FROM THE PRECIPITATE FORMED (**56**), in a test-tube, observe whether it is colored or not,* boil to expel the H_2S which may be present, add a few drops of HNO_3, boil, and observe again the color of the fluid; then cautiously add NH_4OH just to alkaline reaction, heat, observe whether this produces a precipitate, then add some $(NH_4)_2S$, no matter whether ammonia has produced a precipitate or not. **78**

a. NEITHER AMMONIA NOR AMMONIUM SULPHIDE PRODUCES A PRECIPITATE. Pass on to § 188, for iron, nickel, cobalt, zinc, manganese, chromium, aluminium, are not present,† nor are phosphates, borates,‡ silicates, oxalates,§ and fluorides of the alkali-earth metals; **79**

* If the fluid is colorless, it contains no Cr. If colored, the tint will, to some extent, act as a guide to the nature of the substance present; thus a green tint, or a violet tint turning green upon boiling, points to Cr; a light-green tint to Ni; a reddish color to Co; the turning yellow of the fluid upon boiling with nitric acid to Fe. It must, however, be remembered that these tints, except the last, are perceptible only if the metals are present in large quantity, and also that complementary colors, such as, for instance, the green of the Ni solution and the red of the Co solution, will destroy each other, and that, accordingly, a solution may contain both metals and yet appear colorless.

† This only holds good as regards Al and Cr in the absence of non-volatile organic substances, especially acids such as citric and tartaric acids. Citric acid may also prevent the precipitation of Mn. When the preliminary examination has indicated presence of organic matters, and of metals of Groups III. and IV., fuse a portion of the substance with Na_2CO_3 and $NaNO_3$, dissolve in dilute HCl, filter and test the solution according to **78**.

‡ Presence of much NH_4Cl has a great tendency to prevent the precipitation of borates of the alkali-earth metals.

§ Magnesium oxalate is thrown down from HCl solution by NH_4OH after some time only, and never completely; dilute solutions are not precipitated by NH_4OH.

nor silicic acid, originally in combination with other metals.

b. AMMONIUM SULPHIDE PRODUCES A PRECIPITATE, AMMONIA HAVING FAILED TO DO SO: absence of phosphates, borates,* silicates, oxalates,† and fluorides of the alkali-earth metals; of silicic acid, originally in combination with other metals; and also, if no organic matters are present, of iron, chromium and aluminium. Pass on to **82**. **80**

c. AMMONIA PRODUCES A PRECIPITATE before the addition of $(NH_4)_2S$. The course of proceeding to be pursued now depends upon whether, (α) the original solution is simply aqueous, and has a neutral reaction, or (β) the original solution is acid or alkaline. In the former case pass on to **82**, since phosphates, borates, oxalates, silicates, and fluorides of the alkali-earth metals, and silicic acid in combination with other metals, cannot be present. In the latter case regard must be had to the possible presence of all the bodies enumerated in **79**, and also, in the presence of organic matter, of the combinations of alkali-earth metals with citric and tartaric acids; pass on to **94**. **81**

1. DETECTION OF THE BASES OF GROUPS III. AND IV. IF PHOSPHATES, ETC., OF THE ALKALI-EARTH METALS ARE NOT PRESENT.‡ **82**

Mix the fluid mentioned at the beginning of **78**, a portion of which you have submitted to a preliminary examination, with some NH_4Cl, then with NH_4OH, just to alkaline reaction, lastly with $(NH_4)_2S$ until the fluid, after being shaken, smells distinctly of that reagent; shake the mixture until the precipitate begins to separate in flakes, heat gently for some time, and filter.

Keep the FILTRATE,§ which may contain bases of Groups

* Presence of much NH_4Cl has a great tendency to prevent the precipitation of borates of the alkali-earth metals.

† Magnesium oxalate is thrown down from HCl solution by NH_4OH after some time only, and never completely; dilute solutions are not precipitated by NH_4OH.

‡ This simpler method will fully answer the purpose in most cases; for very accurate analysis the method beginning at **94** is preferable, as this will permit also the detection of minute quantities of alkali-earth metals which may have been thrown down together with Al or Cr. Solutions which are distinctly colored by Cr should always be examined by **94**.

§ If the filtrate has a brownish color, this points to Ni, since Ni S, as is well known, under certain circumstances, is slightly soluble in ammonium sulphide; this, however, involves no modification of the analytical course.

II. and I., for subsequent examination according to § 188. Wash the PRECIPITATE with water to which a very little $(NH_4)_2S$ has been added, then proceed with it as follows:

a. IT HAS A PURE WHITE COLOR: absence of iron, cobalt, nickel. You must test it for all the other bases of Groups III. and IV., as the faint tints of chromic hydroxide and manganese sulphide are imperceptible in a large quantity of a white precipitate. Dissolve the precipitate by heating it in a small dish with the least possible amount of HCl; boil—should H_2S be evolved until this is completely expelled—concentrate by evaporation to a small * bulk, add concentrated solution of NaOH in excess, boil for some time. **83**

α. The precipitate formed at first dissolves completely in the excess of soda. Absence of manganese and chromium, presence of aluminium or zinc. Test a portion of the alkaline solution with solution of H_2S (a little, not excess) for ZINC; acidify the remainder with HCl, add NH_4OH *slightly* in excess, and apply heat. A white flocculent precipitate insoluble in more NH_4Cl, indicates ALUMINIUM.† **84**

β. The precipitate formed does not dissolve, or dissolves only partially, in the excess of soda. Dilute, filter, and test the FILTRATE, as in **84**, for ZINC and ALUMINIUM. With the undissolved PRECIPITATE, which, if containing manganese, looks brown, proceed as follows: **85**

aa. If the color of the solution gives you no reason to suspect the presence of chromium, test the precipitate for MANGANESE, with Na_2CO_3 in the outer blowpipe flame.

bb. But where the color of the solution indicates chromium, the examination of the residue insoluble in solution of soda is more complicated, since it may in that case contain also zinc, pos- **86**

* Compare § 106, 6.

† It is of course assumed that the NaOH used is free from aluminium and silicic acid. In default of pure NaOH you may make a counter-experiment with an *equal quantity* of the alkali alone; if you obtain a very much smaller precipitate now than you obtained in the analysis, you may conclude that aluminium is actually present in the substance.

sibly even the whole quantity present of this metal (§ 112). Dissolve the precipitate therefore in H Cl, evaporate the solution to a small residue, dilute, nearly neutralize the free acid with $Na_2 C O_3$ add Ba C O_3 in slight excess, allow to digest in the cold until the fluid has become colorless, filter, and test the precipitate for CHROMIUM, by fusion with $Na_2 C O_3$ and K Cl O_3 (§ 102, 8). Remove the Ba from the filtrate, by precipitating with some $H_2 S O_4$, filter, evaporate to a small residue, add concentrated solution of Na O H in excess, and test the filtrate for ZINC with $H_2 S$, the precipitate, if any, for MANGANESE as in *aa*.

b. IT IS NOT WHITE: this indicates chromium, manga- 87
nese, iron, cobalt, or nickel. If it is black, or inclines to black, one of the three metals last mentioned is present. Under any circumstances all the metals of Groups III. and IV. must be looked for.

Remove the washed precipitate from the filter with a spatula, or by rinsing it with the aid of a wash-bottle through a hole made in the bottom of the filter, into a test-tube, and pour over it rather dilute cold H Cl (1 part of H Cl, sp. gr. 1.12, with about 5 parts of $H_2 O$) in moderate excess.

a. *It dissolves completely* (except perhaps a little 88
sulphur); absence of cobalt and nickel, at least of notable quantities of these two metals.

Boil until the $H_2 S$ is *completely* expelled, add $H N O_3$, boil, filter if particles of sulphur are suspended in the fluid, concentrate by evaporation to a small residue, add concentrated solution of Na O H in excess, boil, filter the fluid from the insoluble precipitate which is sure to remain, wash the latter, and proceed first to examine the filtrate, then the precipitate.

aa. Test a small portion of the *filtrate* with 89
$H_2 S$ for ZINC; acidify the remainder with H Cl, then test with ammonia for ALUMINIUM. Compare **85**.

bb. Dissolve a small portion of the *precipitate* 90
in H Cl, and test with $K_4 Fe (C N)_6$, added drop

by drop, or with K C N S for IRON.* Test another portion for CHROMIUM by fusing with $Na_2 C O_3$, and K Cl O_3, and boiling the fusion with water (§ 102, 8).† If no chromium has been found, examine the remainder for MANGANESE by $Na_2 C O_3$ in the oxidizing flame. If chromium is present, on the other hand, test the remainder of the precipitate for manganese and zinc as directed **86.** (Under these circumstances the whole of the zinc may be present in this precipitate.)

β. The precipitate is not completely dissolved, a **91** *black residue being left.* This indicates COBALT and NICKEL. This indication is not certain, especially in the presence of much Fe S, particles of which may become enveloped in the separated S, and thus be protected from the action of the H Cl. Filter, wash, and examine the filtrate according to **88.** Heat the precipitate with the filter in a porcelain crucible till the filter is incinerated, allow to cool, warm with H Cl and a drop or two of H N O_3, add water, then ammonia in moderate excess, and filter.

The ammoniacal filtrate will be blue in presence of much nickel, brownish in the presence of much cobalt, and will have a less distinct mixed color if both metals are present. Test a portion of it with $(N H_4)_2 S$. If a black precipitate is formed, which does not redissolve on acidifying with H Cl, the presence of cobalt or nickel is proved.

In that case evaporate the rest of the ammoniacal solution to dryness, drive off the ammonia salts by gentle ignition, and proceed with the residue as follows:

aa. Test a small portion of it with borax, first **92** in the outer, then in the inner blowpipe flame. If the bead in the oxidizing flame is violet whilst hot, and of a pale reddish brown when cold, and

* Since Prussian blue dissolves in $K_4 Fe (C N)_6$ to a colorless fluid, small quantities of Fe may easily be overlooked if the reagent is added rapidly in large quantity. The original solution must be tested with $K_6 Fe_2 (C N)_{12}$ and K C N S, to learn whether the Fe be in dyad or tetrad form.

† If the solution is green from the presence of sodium manganate, heat it with a few drops of alcohol and filter off the $Mn O_2$ formed.

turns in the reducing flame gray and turbid, NICKEL is present; but if the color of the bead is blue in both flames, and whether hot or cold, COBALT is present. As in the latter case the presence of nickel cannot be distinctly recognized, examine

bb. the remainder of the residue by dissolving 93
it in H Cl and a little H N O_3, evaporating nearly to dryness, and adding K N O_2, and, lastly, acetic acid (§ 109, 14). If a yellow precipitate forms, after standing for some time at a gentle heat, this confirms the presence of COBALT. Filter after about twelve hours, and test the filtrate with Na O H for NICKEL.

2. DETECTION OF THE METALS OF GROUPS III. AND IV. in 94
CASES WHERE PHOSPHATES, BORATES, OXALATES, SILICATES, FLUORIDES (IN THE PRESENCE OF ORGANIC MATTER, POSSIBLY ALSO TARTRATES AND CITRATES) OF THE ALKALI-EARTH METALS, OR SILICIC ACID MAY POSSIBLY HAVE BEEN THROWN DOWN, *i. e.*, in cases where the original solution was acid or alkaline, and a precipitate was produced by ammonia in the examination of **78**.

Mix the fluid mentioned in **78** with some N H_4 Cl, then with N H_4 O H just to alkaline reaction, lastly with $(N H_4)_2$ S, until the fluid, after being shaken, smells distinctly of the reagent; shake the mixture until the precipitate begins to separate in flakes, heat gently for some time, and filter.

Keep the FILTRATE, which may contain bases of Groups II. and I., for subsequent examination according to § 188. Wash the PRECIPITATE with water to which a very little $(N H_4)_2$ S has been added, then proceed with it as directed **96**. To obtain a clear notion of the obstacles to be overcome in this analytical process, it must be considered that it is necessary to examine the precipitate for the following bodies: Iron, nickel, cobalt (these show their presence to a certain extent by the black or blackish color of the precipitate), manganese, zinc, chromium (the latter generally reveals its presence by the color of the solution), aluminium, barium, strontium, calcium, magnesium, which latter substances may have fallen down in combination with

phosphoric acid, boracic acid, oxalic acid, silicic acid, in form of fluorides, or in combination with chromic oxide. Besides these bodies, silicic acid and free sulphur may be present. (In the presence of organic substances, tartrates and citrates of alkali-earth metals may be also present.)

As the original substance must be afterwards examined **95** for all acids that might possibly be present, it is not *indispensable* to test for the above enumerated acids at this stage; still, as it is often interesting to detect these acids at once, especially in cases where a somewhat large proportion of some alkali-earth metal has been found in this precipitate, a method for the detection of the acids in question will be found appended by way of supplement to the method for the detection of the metals.

As soon as the washing is finished, remove the precipi- **96** tate from the filter with a small spatula, or with the washing-bottle, and pour over it cold dilute H Cl (1 part of H Cl sp. gr. 1.12, with about 5 parts of water) in moderate excess.

a. A RESIDUE REMAINS. Filter, and treat the filtrate **97** as directed **98**. The residue, if it is black, may contain sulphides of nickel and cobalt, and, besides these, sulphur and silicic acid, possibly also calcium fluoride (which is rather difficultly soluble). Wash and examine a sample of it with Na P O_3 before the blowpipe in the outer flame. If a silica skeleton remains undissolved (§ 150, 9) this proves the presence of SILICIC ACID; the color of the bead will generally at once indicate COBALT or NICKEL, compare **92**. Incinerate the rest of the precipitate and test it first for FLUORINE, by heating with H_2 S O_4 (§ 146, 5). If fluorine is present, on treating the residue with a little water, and adding an equal volume of alcohol, CALCIUM sulphate will remain behind. Finally, if the color of the Na P O_3 bead has been ambiguous, remove the alcohol from the sulphuric acid solution by evaporation (if necessary), precipitate the traces of iron generally present by ammonia, and test for nickel and cobalt as in **91** to **94**.

b. NO RESIDUE IS LEFT (except a little sulphur, whose **98** purity is to be proved by washing, drying and burn-

ing): absence of nickel and cobalt, at least in any notable proportion.

Boil the solution until the H_2S is expelled, filter if necessary, and then proceed as follows:

a. Mix a small portion of the solution with dilute 99
H_2SO_4. If a precipitate forms, this may consist of BARIUM and STRONTIUM sulphates, possibly also of calcium sulphate. Filter, wash the precipitate and examine it either by the coloration of flame (see § 99, at end), or decompose it by boiling or fusing with carbonated alkali, wash the carbonates produced, dissolve them in HCl, evaporate to dryness, take up with water, and test the solution as directed **108**. Mix the fluid which has not been precipitated by dilute H_2SO_4, or the fluid filtered from the precipitate produced, with 3 volumes of alcohol. If a precipitate forms, this consists of CALCIUM sulphate. Filter, dissolve in water and add $(NH_4)_2C_2O_4$ to confirm the presence of calcium.

β. Heat a somewhat larger sample with HNO_3, 100
and test a small portion of the fluid with $K_4Fe(CN)_6$ added drop by drop, or with KCNS for IRON; * mix the remainder with Fe_2Cl_6† in sufficient quantity to make a drop of fluid give a yellowish precipitate when mixed on a watch glass with a drop of NH_4OH, evaporate on a water bath to a small bulk, add some water, then a few drops of Na_2CO_3, just sufficient to *nearly* neutralize the free acid, and lastly $BaCO_3$ in slight excess, stir and allow to stand in the cold until the fluid above the precipitate has become colorless. Filter the precipitate (*aa*) from the solution (*bb*), and wash.

aa. Boil the *precipitate* for some time with 101
solution of soda, filter, and test the filtrate for ALUMINIUM, ‡ by acidifying with HCl, adding

* Whether the iron was present as a ferric or a ferrous compound must be ascertained by testing the original solution in HCl with $K_4Fe_2(CN)_{12}$ and KCNS.

† The addition of Fe_2Cl_6 is necessary, to effect the separation of phosphoric acid and silicic acid which may be present, and which would go down in combination with alkali-earth metals on addition of $BaCO_3$.

‡ If the solution or the NaOH contains silicic acid, the precipitate taken for $Al_2(OH)_6$ may also contain silicic acid. A simple trial with $NaPO_3$, on a platinum wire, in the blow-

NH_4OH to alkaline reaction and boiling. The part of the precipitate insoluble in $NaOH$ is examined for CHROMIUM, by fusion with $KClO_3$ and Na_2CO_3 (§ 102, 8).

bb. Mix the *solution* first with a few drops of HCl, boil and precipitate barium from the hot solution by a slight excess of sulphuric acid, filter, make the filtrate alkaline with NH_4OH and add $(NH_4)_2S$.

αα. No precipitate forms: absence of manganese and zinc. Mix the solution with $(NH_4)_2C_2O_4$. If a precipitate of CaC_2O_4 forms, filter and test the filtrate with Na_2HPO_4 for MAGNESIUM. **102**

ββ. A precipitate forms. Filter, and proceed with the filtrate according to **102**. The precipitate may contain MnS, ZnS, traces of CoS and NiS; and also (in the presence of tartrates and citrates of the alkali-earth metals) FeS. Wash it and test for MANGANESE, ZINC, COBALT and NICKEL, according to **87** to **94** (if the last two metals have not been found in **97**). **103**

γ. If you have found alkali-earth metals in *α* and *β*, and wish to know the acids in combination with which they have passed into the precipitate produced by $(NH_4)_2S$, make the following experiments with the remainder of the HCl solution of the $(NH_4)_2S$ precipitate. **104**

αα. Evaporate a small portion in a dish or watch glass on the water bath to complete dryness, then treat with HCl. If there was any SILICIC ACID in the solution, this will be left undissolved. Evaporate the solution with HNO_3 and test it for PHOSPHORIC ACID, by means of molybdic solution (§ 142, 10). **105**

bb. Concentrate another portion by evapora-

pipe flame, will show whether the precipitate really contains Si. Should this be the case, ignite the remainder of the precipitate on the lid of a platinum crucible, add some $Na_2S_2O_7$, fuse and treat with H Cl, which will dissolve the Al, leaving SiO_2 undissolved; precipitate the Al from the solution by NH_4OH.

tion, mix it with solution of Na_2CO_3 *in excess*, boil for some time, filter and examine one portion of the filtrate for OXALIC ACID, by acidifying with acetic acid and adding solution of $CaSO_4$; another portion for BORIC ACID, by slightly acidifying with HCl, and testing with turmeric paper (§ 144 and § 145). (In the presence of organic matter the rest of the filtrate may be used for testing for TARTARIC and CITRIC ACIDS, compare **142**.)

cc. Precipitate the remainder with NH_4OH, **106** filter, wash and dry the precipitate, and examine it for FLUORINE according to § 146, 5.

§ 188.

☞ *Compare the notes on pp.* 422 *and* 434.

(*Separation and Detection of the Metals of Group II. which are precipitated by Ammonium Carbonate in Presence of Ammonium Chloride, viz., Barium, Strontium, Calcium.*)

TO A SMALL PORTION OF THE FLUID IN WHICH AMMONIA AND AMMONIUM SULPHIDE HAVE FAILED TO PRODUCE A PRECIPITATE (**79**), OR OF THE FLUID FILTERED FROM THE PRECIPITATE FORMED, ADD AMMONIUM CHLORIDE, IF THE SOLUTION CONTAINS NO AMMONIUM SALT, THEN AMMONIUM CARBONATE AND SOME AMMONIA, AND HEAT FOR SOME TIME VERY GENTLY (not to boiling).

1. NO PRECIPITATE FORMS: absence of any notable **107** quantity of barium, strontium and calcium. Traces of these metals may, however, be present; to detect them proceed as follows: Add to another portion of the fluid some $(NH_4)_2SO_4$ (prepared by supersaturating dilute H_2SO_4 with NH_4OH); if the fluid becomes turbid, it contains traces of barium. Add to a third portion some $(NH_4)_2C_2O_4$ and allow it to stand; if the fluid turns turbid, traces of calcium are present. Treat the remainder of the fluid as directed § 189, after having removed the traces of Ca and Ba which have been found by means of the reagents that have served for their detection.

2. A PRECIPITATE IS FORMED: presence of CALCIUM, BA- 108
RIUM, or STRONTIUM. Treat the whole fluid of which a portion has been tested with NH_4OH and $(NH_4)_2CO_3$, the same as the sample, filter off the precipitate formed, after gently heating, and test portions of the filtrate with sulphate and oxalate of ammonium for traces of Ca and Ba, which it may possibly still contain; remove such traces, should they be found, by means of the said reagents, and examine the fluid, thus perfectly freed from Ba, Sr and Ca, for magnesium, according to § 189. Wash the precipitate produced by $(NH_4)_2CO_3$, dissolve it in the least possible amount of dilute HCl, evaporate to dryness on the water-bath, take up the residue with *a little* water, and add to a small portion of the fluid a sufficient quantity of solution of $CaSO_4$.

a. No precipitate is formed, NOT EVEN AFTER THE LAPSE OF SOME TIME. Absence of Ba and Sr;* presence of CALCIUM. To confirm mix another sample with $(NH_4)_2C_2O_4$.

b. A precipitate is formed by solution of calcium sulphate.

α. It is formed immediately: this indicates BA- 109
RIUM. Besides this, Sr and Ca may also be present.

Evaporate the remainder of the HCl solution of the precipitate produced by $(NH_4)_2CO_3$ to dryness, digest the residue with strong alcohol, decant the fluid from the undissolved $BaCl_2$, dilute with an equal volume of water, mix with a few drops of SiH_2F_6—which will throw down the small portion of barium that had dissolved as $BaCl_2$—allow to stand for some time; filter, and mix the filtrate with dilute H_2SO_4. The formation of a precipitate indicates the presence of strontium or calcium, or of both. Filter after some time, and test the precipitate according to p. 130 for STRONTIUM and CALCIUM. The separation by boiling the sulphates with $(NH_4)_2SO_4$ suffices for ordinary cases; but in very delicate analyses the nitrates must be

* Very minute traces of Sr cannot be detected in this way, as $SrSO_4$ is not absolutely insoluble. See § 99.

treated with alcohol and ether, and the residue examined in the spectroscope.

β. It is formed only after some time. Absence of barium, presence of STRONTIUM. Mix the remainder of the aqueous solution of the chlorides with a sufficient amount of concentrated solution of $(NH_4)_2SO_4$, and boil for some time, renewing the water as it evaporates, and adding ammonia to keep the fluid alkaline. Then filter off the $SrSO_4$, and test the filtrate for CALCIUM, with $(NH_4)_2C_2O_4$. 110

§ 189.

(*Examination for Magnesium.*)

TO A PORTION OF THE FLUID IN WHICH CARBONATE, SULPHATE, AND OXALATE OF AMMONIUM HAVE FAILED TO PRODUCE A PRECIPITATE (107) OR OF THE FLUID FILTERED FROM THE PRECIPITATES FORMED (108), ADD AMMONIA, THEN SOME SODIUM PHOSPHATE, AND, SHOULD A PRECIPITATE NOT AT ONCE FORM, RUB THE INNER SIDES OF THE TEST-TUBE WITH A ROD, AND LET THE MIXTURE STAND FOR SOME TIME.

1. NO PRECIPITATE IS FORMED: absence of magnesium. Evaporate another portion of the fluid to dryness (preferably in the lid of a platinum crucible), and ignite gently. *If a residue remains,* treat the remainder of the fluid the same as the sample, and examine the residue (freed from ammonia by the moderate ignition) for potassium and sodium, according to § 190. *If no residue is left,* this is proof of the absence of K, Na and Li; pass on at once to § 191. 111

2. A CRYSTALLINE PRECIPITATE IS FORMED: presence of MAGNESIUM.* As testing for alkalies can proceed with certainty only after the removal of magnesium, evaporate the remainder of the fluid to dryness, and ignite until all 112

* $NH_4MgPO_4 . 6H_2O$ is invariably crystalline; if Na_2HPO_4 produces a slight flocculent precipitate, you are therefore not justified in concluding that magnesium is present. The slight flocculent precipitate which is here sometimes obtained, consists of $AlPO_4$. You get it when Al is contained in the original substance, and you use too large an excess of ammonia in precipitating the third and fourth groups. Its production depends upon the fact that $AlPO_4$ is far less soluble in ammonia than $Al(OH)_3$. $AlPO_4$ differs also from $MgNH_4PO_4$ by its insolubility in acetic acid. If you want to test the precipitate in this manner, it should first be filtered off. From the acetic acid solution of $MgNH_4PO_4$, ammonia would throw down the pure salt.

ammonium salts are removed. Warm the residue with some water, add baryta water (prepared from the crystals) * as long as a precipitate continues to form, boil, filter, add to the filtrate a mixture of $(NH_4)_2CO_3$ and NH_4OH in slight excess, heat for some time gently, filter, evaporate the filtrate to dryness, with addition of some NH_4Cl (to convert into chlorides the alkali hydroxides or carbonates that may happen to form), ignite gently, dissolve in a little water, precipitate if necessary once more with $(NH_4)_2CO_3$ and NH_4OH, filter, evaporate again, and if a residue remains, ignite this gently, not above faint redness, and examine it according to § 190.

§ 190.

(Examination for Potassium and Sodium.)

YOU HAVE NOW TO EXAMINE FOR POTASSIUM AND SODIUM THE GENTLY IGNITED RESIDUE, FREE FROM AMMONIUM SALTS AND ALKALI-EARTH METALS, WHICH HAS BEEN OBTAINED IN **111** or **112**. Dissolve it in a little water, filter if necessary, evaporate until there is only a small quantity of fluid left.

1. Bring a portion of the concentrated solution into the lamp flame by means of a loop of platinum wire. A strong yellow coloration indicates SODIUM. **113**

2. To the remainder of the solution add, after cooling, a few drops of H_2PtCl_6. If a yellow crystalline precipitate forms immediately, or after some time, POTASSIUM is present. Should no precipitate form, evaporate to dryness at a gentle heat, and treat the residue with a very small quantity of water, or, if chlorides alone are present, with a mixture of water and alcohol, when the presence of minute traces of K will be revealed by a small quantity of a heavy yellow powder being left undissolved (§ 89, 3). In the presence of an iodide the deep brown color of the fluid interferes with the detection of K by H_2PtCl_6; under these circumstances test with *acid sodium tartrate*. **114**

* Or thin milk of lime, freed from every trace of alkali by repeated extraction with water. Add it to the warm fluid with stirring till turmeric paper is strongly affected.

§ 191.

(Examination for Ammonium.)

THERE REMAINS STILL THE EXAMINATION FOR AMMONIUM. 115 Triturate some of the substance with an excess of Ca $(OH)_2$ and, if necessary, a little water. If the escaping gas smells of ammonia, if it blues moist red litmus paper, and forms white fumes with H Cl vapors, brought into contact with it by means of a glass rod, AMMONIUM is present. The reaction is the most sensitive if the trituration is made in a small beaker, and the latter covered with a glass plate with a slip of moist turmeric or red litmus paper adhering to the under side.

A, 1. SUBSTANCES SOLUBLE IN WATER.

DETECTION OF ACIDS.

☞ *Consult also the Notes in the Third Section, p.* 423.

I. *In the Absence of Organic Acids.*

§ 192.

Consider, in the first place, which are the acids that form with the bases found compounds soluble in water, and let this guide you in the examination. To students the table given in Appendix IV. will prove of considerable assistance (see also **30**). The following plan of examination works best when the acids are combined exclusively with alkali or alkali-earth metals; it is therefore sometimes advisable to precipitate any heavy metals present by H_2S or $(NH_4)_2S$ before proceeding. The sulphides should be filtered off and the excess of H_2S removed by boiling, or of $(NH_4)_2S$ by acidifying with H Cl, boiling and filtering off the sulphur. It must not be forgotten that sulphur, hydrochloric acid, chromic acid, and chloric acid cannot be looked for in this fluid, and also that the results of the testing for sulphuric and nitric acids will not be so trustworthy.

In absence of sulphides and sulphur salts, most of the acids (see § 145, 8) may also be obtained as sodium salts

by boiling,* in a platinum dish, the original solution, with a moderate excess of $Na_2 C O_3$ and filtering from the precipitate. A portion of the filtrate should be heated to boiling, and very slightly acidified with $H N O_3$ for treatment according to **116**, 2. To be sure that all $Na_2 C O_3$ is decomposed, see that litmus paper, which has been reddened by the liquid, remains red when dried.

[Generally, the *best* method for removing those bases which interfere with the detection of acids, is to fuse the substance with $Na_2 C O_3$ (sometimes with a little $Na N O_3$), as given for insoluble substances, in § 194. Solutions must of course be first evaporated to dryness, with previous neutralization by $Na_2 C O_3$ if free acid is present.]

1. THE ACIDS OF ARSENIC, CARBONIC ACID, SULPHUR combined with metals or hydrogen, CHROMIC ACID, and SILICIC ACID will have been usually detected in the examination for metals, see **20** and **35**.† Chromic acid is also easily recognized by the yellow or reddish-yellow color of the solution. If in doubt, test for it with $Pb (C_2 H_3 O_2)_2$ and $C_2 H_4 O_2$ (§ 138, 8) or—for very minute quantities—with decoction of logwood (§ 138, 12). **116**

2. Add to a portion of the solution $Ba Cl_2$, or, if lead, silver, or mercurous salts are present, $Ba (N O_3)_2$, and should the reaction of the fluid be acid, add $N H_4 O H$ to neutral or slightly alkaline reaction.

a. NO PRECIPITATE IS FORMED: absence of sulphuric, phosphoric, chromic, silicic, oxalic, arsenious, and arsenic acids, as well as of notable quantities of boric and hydrofluoric acids.‡ Pass on to **119**. **117**

b. A PRECIPITATE IS FORMED. Dilute the fluid, and **118**

* In all cases until no more $C O_2$ escapes, and if $N H_4$ salts are present, until $N H_3$ ceases to be given off from the liquid, kept alkaline.

† ARSENIOUS ACID and ARSENIC ACID are distinguished from each other by their reaction with $Ag N O_3$, or with $Na O H$, and $Cu SO_4$ (see § 134, 9).

CARBONIC ACID and SULPHUR in combination with metals betray their presence by effervescing upon the addition of $H Cl$; the escaping gases may be distinguished from one another by the smell. The presence of carbonic acid may be confirmed by lime water (see § 149), and that of hydrosulphuric acid by lead acetate (§ 156). Free carbonic acid and free hydrosulphuric acid in aqueous solution may be detected by the same reagents.

‡ If the solution contains an ammonium salt in somewhat considerable proportion, the non-formation of a precipitate cannot be considered a conclusive proof of the absence of these acids, since the barium salts of most of them (not the sulphate) are in presence of ammonium salts more or less soluble in water.

add H Cl or, as the case may be, HNO_3; if the precipitate does not redissolve, or at least not completely, SULPHURIC ACID is present.

3. Add $AgNO_3$ to a portion of the solution. If this 119
fails to produce a precipitate, test the reaction, and if acid, add to the fluid some dilute NH_4OH, taking care to add the reagent so cautiously that the two fluids do not intermix; if the reaction is alkaline, on the other hand, add with the same care some dilute HNO_3, and watch attentively whether a precipitate or a cloud will form at the junction of the two fluids.

a. NO PRECIPITATE IS FORMED AT THE JUNCTION OF 120
THE TWO FLUIDS, EITHER IMMEDIATELY OR AFTER SOME TIME. Pass on to **125**; there is neither chlorine, bromine, iodine, cyanogen,* ferro- and ferricyanogen, nor sulphur present; nor phosphoric, arsenic, arsenious, chromic, silicic, oxalic acids, nor boric acid, if the solution was not too dilute.

b. A PRECIPITATE IS FORMED. Observe the color† of 121
it, then add HNO_3, and shake the mixture.

α. The precipitate dissolves completely: absence of chlorine, bromine, iodine, cyanogen, ferro- and ferricyanogen, and also of sulphur. Pass on to **125**.

β. A residue is left: chlorine, bromine, iodine, 122
cyanogen, ferro- or ferricyanogen may be present; and if the residue is black or blackish, HYDROSULPHURIC ACID or a soluble METALLIC SULPHIDE. The presence of sulphur may, if necessary, be readily confirmed, by mixing another portion of the solution with $CuSO_4$, or with a solution of $Pb(OH)_2$ in NaOH.

aa. Test another portion of the fluid for IODINE and subsequently for BROMINE, by the methods described in § 157.

bb. Test a small portion of the fluid with 123

* That the cyanogen in mercuric cyanide is not indicated by $AgNO_3$ has been mentioned § 155, 11.

† Chloride, bromide, cyanide, ferrocyanide, oxalate, silicate and borate of silver are white; iodide, orthophosphate and arsenite of silver are yellow; arsenate and ferricyanide of silver are brownish-red; silver chromate is purple-red; silver sulphide, black.

$Fe_2 Cl_6$ for FERROCYANOGEN; and, if the color of the silver precipitate leads you to suspect the presence of FERRICYANOGEN, test another portion for this latter substance with $Fe S O_4$ (freshly prepared, by warming iron wire with dilute $H_2 S O_4$). If the original solution has an alkaline reaction, some H Cl must be added before the addition of the ferric or ferrous salt.

cc. CYANOGEN, if present in form of a simple cyanide of an alkali metal soluble in water, may usually be readily recognized by the smell of hydrocyanic acid, which the substance emits, and which is rendered more strongly perceptible by addition of a little dilute $H_2 S O_4$. If ferrocyanogen and ferricyanogen are absent, cyanogen may be detected by the method given in § 155, 6. If they are present see § 219.

dd. Should bromine, iodine, cyanogen, ferro- **124**
cyanogen, ferricyanogen, and sulphur not be present, the precipitate which nitric acid has failed to dissolve consists of silver CHLORIDE.

But where one or other of these bodies is present, a special examination for chlorine may become necessary, particularly when the quantity of the precipitate does not afford a decided indication.* See § 157.

4. CHLORIC ACID is known by the yellow color produced **125** when a little of the solid substance is brought into contact with concentrated $H_2 S O_4$ (§ 160).

5. NITRIC ACID is tested for with $Fe S O_4$ and $H_2 S O_4$ (§ 159). The presence of certain other acids (chloric, chromic, hydriodic) impedes this reaction. If such acids are present they must be destroyed or removed. Chloric acid is destroyed by ignition (§ 161, at the end), chromic acid is reduced by sulphurous acid, chromic hydroxide being precipitated afterwards with ammonia; hydriodic acid is removed by silver sulphate.

You have still to test for phosphoric acid, boric acid,

* Supposing, for instance, $Ag N O_3$ to have produced a copious precipitate insoluble in nitric acid, and the subsequent examination to have shown mere traces of I and Br, the presence of Cl may be held to be demonstrated, without requiring additional proof.

silicic acid and oxalic acid, as well as for hydrofluoric acid.

For the first four acids test only in cases where both $Ba\,Cl_2$ and $Ag\,N\,O_3$ have produced precipitates in neutral solutions. Compare also foot-note to **117.**

6. Test for PHOSPHORIC ACID, by adding to a portion of **126** the fluid $N\,H_4\,O\,H$ in excess, then $N\,H_4\,Cl$ and $Mg\,S\,O_4$ mixture (§ 142, 7). Very minute quantities of phosphoric acid are detected most readily by means of molybdic solution (§ 142, 10). Arsenic acid, if present, must be first separated by $H_2\,S$, the solution being acidified and kept at 70° during the passage of the gas.

7. To detect OXALIC ACID and HYDROFLUORIC ACID, add $Ca\,Cl_2$ to a fresh portion of the solution. If the reaction of the fluid is acid, add ammonia to alkaline reaction. If the $Ca\,Cl_2$ produces a precipitate which is not redissolved by addition of acetic acid, one or both bodies are present. Examine now a sample of the original substance* for fluorine according to § 146, 5, another sample for oxalic acid according to § 145, 7.

8. Acidulate a portion of the fluid slightly with $H\,Cl$, **127** then test for BORIC ACID, by means of turmeric paper (§ 144, 7). Chloric, chromic, and hydriodic acids impede the reaction. If present, they must be removed or destroyed as directed **125.**

9. Should SILICIC ACID not yet have been found in the course of testing for the bases, acidulate a portion of the fluid with $H\,Cl$, evaporate to dryness, and treat the residue with $H\,Cl$ (§ 150, 2).

A, 1. SUBSTANCES SOLUBLE IN WATER.

DETECTION OF ACIDS.

II. *In Presence of Organic Acids.*

§ 193.

1. The examination for the INORGANIC ACIDS, including **128** oxalic acid, is made as described § 192. As the tartrates and citrates of barium and silver are insoluble, or diffi-

* If boric acid is present, use instead of original substance, the precipitate by $Ca\,Cl_2$ which is free from boron.

cultly soluble in water, tartaric acid and citric acid can be present only in cases where both $BaCl_2$ and $AgNO_3$ have produced precipitates in the neutral fluid; still bear in mind that these salts are slightly soluble in solutions of ammonium salts.

Before testing for the ORGANIC ACIDS, remove Groups III.–VI., as follows:—Where the metal belongs to Group V. or Group VI. the removal is effected by H_2S, where it belongs to Group IV. by $(NH_4)_2S$. After filtering off the sulphides, and removing the excess of $(NH_4)_2S$ by acidifying with HCl, heating, and filtering off the S, proceed to **129.** Where the metal is aluminium or chromium, try first to precipitate these substances by boiling with Na_2CO_3; should this fail, as it will where the acid is non-volatile, precipitate the latter in a fresh portion of the solution with normal lead acetate, wash the precipitate, diffuse it through water, pass H_2S, filter off the PbS, and treat the filtrate as directed **129.** To separate acetic or formic acid from metals which lie in the way of their detection, you may also distil the salt with dilute H_2SO_4.

129 2. Make a portion of the fluid feebly alkaline with ammonia, add some NH_4Cl, then a sufficient quantity of $CaCl_2$, shake vigorously, and let the mixture stand from ten to twenty minutes.

a. NO PRECIPITATE IS FORMED, EVEN AFTER THE LAPSE OF SOME TIME. Absence of tartaric acid; pass on to **130.**

b. A PRECIPITATE IS FORMED, IMMEDIATELY, OR AFTER SOME TIME. Filter, and keep the filtrate for further examination according to **130.** Wash the precipitate, digest and shake it with solution of NaOH, without applying heat, then dilute with a little water, filter, and boil the filtrate some time. If a precipitate separates, TARTARIC ACID is indicated. Filter hot, and test the precipitate with ammonia and $AgNO_3$ (§ 163, 8).

130 3. Mix the fluid in which $CaCl_2$ has failed to produce a precipitate, or that which has been filtered from the precipitate formed—in which latter case some more $CaCl_2$ is to be added—with 3 measures of alcohol.

a. No PRECIPITATE IS FORMED. Absence of citric, malic, and succinic acids. Pass on to **134.** **131**

b. A PRECIPITATE IS FORMED. Filter and treat the filtrate as directed **134.** Treat the precipitate as follows: **132**

Wash with alcohol, dissolve on the filter in a little dilute H Cl, add ammonia to the filtrate to alkaline reaction, and boil for some time.

α. IT REMAINS CLEAR. Absence of citric acid. Add more alcohol, filter off the precipitate, which may contain malate and succinate of calcium, wash it a little with alcohol, dissolve in a porcelain dish in a sufficient quantity of strong HNO_3, and evaporate to dryness on the water-bath. Succinic acid will remain unchanged, malic acid is converted into oxalic acid with evolution of CO_2. Boil the residue with excess of solution of Na_2CO_3, filter, neutralize exactly with H Cl, heat to remove CO_2, and mix a small portion of the fluid with solution of $CaSO_4$. If a white precipitate is formed of CaC_2O_4, MALIC ACID is indicated. If malic acid is indicated, prepare some more of the calcic precipitate, and confirm by testing it according to § 166; also test for succinic acid by mixing the rest of the fluid with excess of $CaCl_2$, filtering, and adding alcohol to the filtrate; a precipitate indicates SUCCINIC ACID. If malic acid has not been found, test the rest of the neutralized fluid for SUCCINIC ACID with Fe_2Cl_6 (§ 168).

β. A HEAVY WHITE PRECIPITATE IS FORMED. Presence of CITRIC ACID. Filter boiling, and test the filtrate for malic and succinic acids as in *α*. To remove all doubt whether the precipitate is calcium citrate, redissolve it in H Cl, heat, supersaturate again with NH_4OH, and boil; the precipitate will now be thrown down again. (Compare § 164, 3.) **133**

4. Heat the filtrate of **132**, or the fluid in which addition of alcohol has failed to produce a precipitate (**131**), to expel the alcohol, neutralize *exactly* with H Cl, and add Fe_2Cl_6. If this fails to produce a light-brown floc- **134**

culent precipitate, benzoic acid is absent. If a precipitate of the kind is formed, filter, and heat the washed precipitate with ammonia in excess; filter, evaporate the filtrate nearly to dryness, and test for BENZOIC ACID with H Cl (§ 169, 2). Benzoic acid may generally be readily detected in the original substance, by treating a small portion with dilute H Cl, which will leave the benzoic acid undissolved; it is then filtered off and heated on platinum foil (§ 169, 1).

5. Evaporate a portion of the solution to dryness—if **135** acid, after previous saturation with soda—introduce the residue or a portion of the original dry substance into a test-tube, pour some alcohol over it, add about an equal volume of concentrated H_2SO_4, and heat to boiling. Evolution of the odor of acetic ether demonstrates the presence of ACETIC ACID. The odor is rendered more distinctly perceptible by shaking the cooling or cold mixture.

6. Test for FORMIC ACID by just acidifying a portion **136** with H Cl (if not acid already), adding $HgCl_2$ and heating. A white turbidity from the separation of Hg_2Cl_2 indicates formic acid (§ 172, 6). Confirm by $AgNO_3$, and by $Hg_2(NO_3)_2$ (§ 172).*

A, 2. SUBSTANCES INSOLUBLE IN WATER, BUT SOLUBLE IN HYDROCHLORIC ACID, NITRIC ACID, OR NITRO-HYDROCHLORIC ACID.

DETECTION OF THE ACIDS.

I. *In Absence of Organic Acids.*

§ 194.

In the examination of these compounds attention must be directed to all inorganic acids, with the exception of chloric acid. Cyanogen compounds and silicates are not examined by this method. (Compare § 197 and § 198.)

* In the presence of chromic or chloric acid the reduction of the silver and mercury does not take place. If chromic acid is present, mix the original solution with sulphuric acid, add excess of lead oxide and shake, filter, mix the filtrate with excess of dilute sulphuric acid, and distil. Test the distillate as above. If chloric acid is present, saturate the acids with lead oxide, and treat with alcohol; the formate is insoluble, the chlorate soluble. If tartaric acid is present it will also be safer to mix the fluid with dilute H_2SO_4 and distil off the formic acid.

1. CARBONIC ACID, SULPHUR (in the form of metallic sul- 137.
phides), ARSENIOUS ACID, ARSENIC ACID, and CHROMIC ACID, if present, have been found already in the examination for bases; NITRIC ACID, if present, has been detected in the preliminary examination, by the ignition in a glass tube (8).

2. Mix a sample of the substance with 4 parts of pure 138
Na_2CO_3 and should a metallic sulphide be present, add some $NaNO_3$; fuse the mixture in a platinum crucible if there are no reducible metallic compounds present, in a porcelain crucible if such compounds are present; boil the fused mass with water, and add a little HNO_3, leaving the reaction of the fluid, however, still alkaline; heat again, filter, and proceed with the filtrate according to § 192.*

3. As the phosphates of the alkali-earth metals are 139
only incompletely decomposed by fusion with Na_2CO_3, it is always advisable in cases where alkaline earths are present, and phosphoric acid has not yet been detected, to dissolve a fresh sample of the substance in HNO_3, and test for PHOSPHORIC ACID with molybdic solution (§ 142, 10). In the presence of silicic or arsenic acid, prepare a solution with HCl, separate these acids, add HNO_3, evaporate nearly to dryness, dilute with water containing HNO_3, and then test with molybdic solution.

4. If in the examination for bases, alkali-earth metals have been found, it is also advisable to test a separate portion for FLUORINE, by § 146, 5.

5. That portion of the substance which has been 140
treated as directed in **138**, can be tested for SILICIC ACID only in cases where the fusion has been effected in a platinum crucible; when a porcelain crucible has been used, examine a separate portion by evaporating the HCl or HNO_3 solution (§ 150, 3).

6. Examine a separate portion of the substance for OXALIC ACID by boiling with Na_2CO_3, see **142**. Acidify the alkaline filtrate with acetic acid and test with solution of $CaSO_4$. If a pulverulent precipitate is formed, this indicates oxalic acid. Confirm by taking a fresh portion

* In the presence of a metallic sulphide, a separate portion of it must be examined for sulphuric acid, by heating it with HCl, filtering, diluting the filtrate, and adding $BaCl_2$.

of the substance, removing CO_2 if necessary by dilute H_2SO_4, and then testing according to § 145, 7.

A, 2. SUBSTANCES INSOLUBLE IN WATER, BUT SOLUBLE IN HYDROCHLORIC ACID, NITRIC ACID, OR NITRO-HYDROCHLORIC ACID.

DETECTION OF THE ACIDS.

II. *In Presence of Organic Acids.*

§ 195.

1. Conduct the examination for INORGANIC ACIDS according to § 194. **141**

2. Test for ACETIC ACID as directed § 171, 7.

3. To a small portion of the substance in a watch-glass add a little dilute HCl. If a residue remains, this should be tested for BENZOIC ACID by heating. Any considerable quantity of this acid is most readily detected in this way, but a small quantity might completely dissolve; it is therefore necessary to recur to this acid in **142.**

4. Boil a portion of the substance for a few minutes with a large excess of solution of Na_2CO_3, adding some of the solid if the solution is not strong, and filter. You will now have all the organic acids in the filtrate as sodium salts. Evaporate the filtrate to concentrate it, acidify with HCl, heat to drive off CO_2 and proceed according to **129.** If any heavy metals have passed into solution through the agency of organic acids, these must first be removed by H_2S or $(NH_4)_2S$. **142**

B. SUBSTANCES INSOLUBLE OR SPARINGLY SOLUBLE IN WATER, HYDROCHLORIC ACID, NITRIC ACID, AND NITRO-HYDROCHLORIC ACID.

DETECTION OF THE BASES, ACIDS, AND NON-METALLIC ELEMENTS.

§ 196.

☞ *Compare the Notes in the third Section, p. 434.*

To this class belong the following bodies: **143**

BARIUM SULPHATE, STRONTIUM SULPHATE, and CALCIUM SULPHATE.*

* Calcium sulphate passes partially into the solution effected by water, and often completely into that effected by acids.

LEAD SULPHATE * and LEAD CHLORIDE.†

SILVER CHLORIDE, silver bromide, silver iodide, silver cyanide,‡ silver ferro- and ferricyanide.§

SILICIC OXIDE, SILICIC ACID, and many SILICATES.

Native and ignited ALUMINA, and many aluminates.

Ignited chromic oxide and CHROMIC IRON (a compound of chromic oxide and ferrous oxide).

Ignited and native stannic oxide (tin-stone).

Some metaphosphates and some arsenates.

CALCIUM FLUORIDE and a few other compounds of fluorine.

SULPHUR.

CARBONACEOUS MATTER.

Of these compounds those printed in small capitals are more frequently met with. To the silicates a special chapter (§§ 198–201) is devoted.

The substance is in the first place subjected to the preliminary experiments described below in *a*–*c*, unless the quantity at disposal is too small, when you at once pass on to **149**, bearing in mind, however, that the substance may contain all the aforesaid bodies.

a. Examine attentively the physical condition of the **144** residue to ascertain whether it is homogeneous or not, whether it is sandy or pulverulent, whether it has the same color throughout, or is made up of variously colored particles, etc. A microscope, or at least a lens, will be often found needful for this purpose.

b. Heat a small sample in a glass tube sealed at one **145** end. If brown fumes arise, and SULPHUR sublimes, this is of course a proof of the presence of that substance.

c. If the substance is black, this indicates, in most **146** cases, the presence of CARBONACEOUS MATTER (charcoal, coal, bone-black, lamp-black, graphite, etc.) Heat a small sample on platinum foil over the blowpipe flame;

* Lead sulphate may pass completely into the solution effected by acids.

† Lead chloride can here only be found if the precipitate insoluble in acids has not been thoroughly washed with hot water.

‡ Bromide, iodide, and cyanide of silver are decomposed by boiling with nitro-hydrochloric acid, and converted into silver chloride: they can accordingly be found here only in cases where the operator has to deal with a substance which—as nitro-hydrochloric acid has failed to effect its solution—is examined directly by the method described here.

§ With regard to the examination of these compounds, compare also § 197.

if the black substance is consumed, it consisted of CARBON in some shape or other. Graphite (which may be readily recognized by its property of communicating its color to the fingers, to paper, etc.) requires the aid of oxygen for its combustion.

d. Heat a small sample with a small lump of K C N and some water, for some time, filter, and test the filtrate with $(N H_4)_2 S$. A brownish-black precipitate indicates SILVER. **147**

e. If an undissolved residue has been left in *d*, wash this thoroughly with water, and if white, moisten it with $(N H_4)_2 S$; if it turns black, LEAD salts are present. If, however, the residue left in *d* is black, heat it with some ammonium acetate, adding a few drops of acetic acid, filter, and test the filtrate for LEAD, by means of $H_2 S O_4$ and $H_2 S$.* **148**

The results obtained by these preliminary experiments serve as a guide in the following course:

1. *a.* LEAD SALTS ARE NOT PRESENT. Pass on to **150.**

   b. LEAD SALTS ARE PRESENT. Heat the substance repeatedly with a concentrated solution of ammonium acetate until the lead salt is completely dissolved out. Test a portion of the filtrate for CHLORINE, another for SULPHURIC ACID, and the remainder for LEAD, the last by addition of $H_2 S O_4$ in excess, and by $H_2 S$. If ammonium acetate has left a residue, wash this, and treat it as directed **150.** **149**

2. *a.* SILVER SALTS ARE NOT PRESENT. Pass on to **151.**

   b. SILVER SALTS ARE PRESENT. Digest the substance free from lead repeatedly with K C N and water, at a gentle heat (in presence of sulphur, in the cold), until all the silver salt is removed. If a *residue* is left, wash this, and proceed with it according to **151.** Of the *filtrate*, which contains K C N, mix the larger portion with $(N H_4)_2 S$ to precipitate the silver. Wash the precipitated $Ag_2 S$, then dissolve in $H N O_3$, dilute the solution and add H Cl, to ascertain whether the precipitate really consisted of $Ag_2 S$. Test another small portion of the filtrate for SULPHURIC ACID.† **150**

* The presence of lead in silicates, *e.g.*, in glass, cannot be detected by this method.

† As the $K_2 C O_3$ contained in the K C N may have produced a total or partial decomposition of sulphates of the alkali-earth metals.

3. *a.* SULPHUR IS NOT PRESENT. Pass on to **152.**

b. SULPHUR IS PRESENT. Heat the substance free **151**
from silver and lead in a covered porcelain crucible until all the sulphur is expelled, and if a residue is left, treat this according to **152.**

4. Mix the substance free from silver, lead, and sul- **152**
phur with 4 parts of $Na_2 C O_3$, and one part of $K N O_3$,* heat in a platinum crucible until the mass is in a state of calm fusion, place the red-hot crucible on a thick cold iron plate to cool. You will thus generally succeed in removing the fused mass from the crucible in a cake. Soak the mass now in water, boil, filter, and wash the residue until $Ba Cl_2$ no longer produces a precipitate in the washings. (Add only the first washings to the filtrate.)

a. The solution so obtained contains the acids which **153**
were present in the substance decomposed by fusing. But it may, besides these acids, contain also such bases as are soluble in caustic alkalies. Proceed as follows:

α. Test a small portion for SULPHURIC ACID.

β. Test another portion (after acidifying with $H N O_3$) with molybdic solution for PHOSPHORIC ACID and ARSENIC ACID (§ 142, 10). If a yellow precipitate forms, test for arsenic acid with $H_2 S$, and remove it by the same means if present, separate silicic acid if present, and then test again for phosphoric acid.

γ. Test another portion for FLUORINE (§ 146, 7).

δ. If the solution is yellow, CHROMIC ACID is present. To confirm, acidify a portion of the solution with acetic acid, and test with lead acetate.

ε. Acidify the remainder with H Cl, evaporate **154**
to dryness, and treat the residue with H Cl and water. If a residue is left which refuses to dissolve even in boiling water, this consists of SILICIC

* Addition of $K N O_3$ is useful even in the case of white powders, as it counteracts the injurious action of lead silicate, should any be present, upon the platinum crucible. In the case of black powders the proportion of $K N O_3$ must be correspondingly increased, in order that carbon, if present, may be consumed as completely as possible, and that any chromic iron present may be more thoroughly decomposed.

ACID. Test the H Cl solution now in the usual way for those bases which, being soluble in caustic alkalies, may be present.

b. Dissolve *the residue left in* **152** in H Cl (effer- **155** vescence indicates the presence of alkali-earth metals —a residue insoluble in H Cl would have to be examined according to § 130, 8, as it might be STANNIC OXIDE), and test the solution for the bases as directed in § 183. (If much silicic acid has been found in **154**, it is advisable to evaporate the solution of the residue to dryness, and to treat with H Cl and water, in order that the silicic acid remaining may also be removed as completely as possible.)

5. If you have found in 4 that the residue insoluble in **156** acids contains a silicate, treat a separate portion of it according to **157**, to ascertain whether this silicate contains alkalies.

6. If a residue is still left undissolved upon treating **157** the residue left in **152** with H Cl (**155**), this may consist either of silicic acid which has separated, or of an undecomposed portion of barium sulphate; it may, however, also be calcium fluoride, and if it is dark colored, chromic iron, as the last-named two compounds are only with difficulty decomposed by the method given in (**152**). As to calcium fluoride, it may be easily decomposed by H_2SO_4. Chromic iron is best treated as follows: Fuse 12 parts of sodium disulphate and project 1 part of the finely powdered mineral into the crucible, stir often and keep up the heat for half an hour, first gently, then raising it till sulphuric oxide is no longer driven off. Add 6 parts of sodium carbonate, fuse, add gradually 6 parts of potassium nitrate, and after some time increase the heat, stirring diligently with a platinum wire. Finally allow to cool and boil with water.

7. If the residue insoluble in acids contained silver, **158** you have still to ascertain whether that metal was present in the original substance as chloride, bromide, iodide, etc., or whether it has been converted into chloride by the treatment employed to effect the solution of the original substance. For that purpose treat a portion of the original substance with boiling water until the

soluble part is completely removed; then treat the residuary portion in the same way with dilute HNO_3, wash the undissolved residue with water, and test a small sample of it for silver according to **147**. If silver is present, proceed to ascertain the acid radical with which the metal is combined; this may easily be effected by boiling the remainder of the residue with rather dilute solution of soda, filtering, and testing the filtrate, after acidifying it, for ferro- and ferricyanogen. Digest the washed residue now with finely granulated zinc and water, with addition of some H_2SO_4, and filter after the lapse of ten minutes. You may now at once test the filtrate for chlorine, bromine, iodine and cyanogen; or you may first throw down the zinc with Na_2CO_3, in order to obtain the acid radicals in combination with sodium.

SECTION II.

PRACTICAL COURSE IN PARTICULAR CASES.

I. Analysis of Cyanides, Ferrocyanides, etc., insoluble in water, and also of Mixed substances containing such Compounds.

☞ *Compare the Notes in Section III., p. 435.*

§ 197.

The analysis of ferrocyanides, ferricyanides, etc., by **159** the common method is often attended by the manifestation of such anomalous reactions as easily to mislead the analyst. Moreover, acids often fail to effect the complete solution of these compounds. For these reasons it is advisable to analyze them, and mixtures containing them, by the following special method:

1. Treat the substance with water until the soluble parts are entirely removed, and boil the residue with strong solution of NaOH; after a few minutes' ebullition add some Na_2CO_3, and boil again for some time; filter, should a residue remain, and wash the latter.

a. The residue, which is now free from cyanogen, unless the substance contains Ag C N, is examined by the usual method, beginning at **35.** **160**

b. The solution, which, if combinations of compound cyanogen radicals (ferrocyanogen, cobalticyanogen, etc.), are present, contains these combined with alkali metals, may also contain other acids, which have been separated from their bases by boiling with $Na_2 C O_3$, and lastly, also, such hydroxides as are soluble in caustic alkalies. Treat it as follows: **161**

α. Mix the alkaline fluid with $H_2 S$ to test for metals of the fourth and fifth groups.* **162**

aa. No permanent precipitate is formed. Absence of zinc and lead. Pass on to **163.**

bb. A permanent precipitate is formed. Add to the fluid a little yellow sodium sulphide, drop by drop, until the metals of the fourth and fifth groups present in the alkaline solution are just thrown down, heat moderately, filter, and treat the filtrate as directed **163.** Dissolve the washed precipitate in $H N O_3$, which may leave Hg S behind, and examine the solution for copper and lead, as well as for zinc and other metals of the fourth group, which may, in the same way as copper, have passed into the alkaline solution, by the agency of organic matters.

β. To test the alkaline fluid, which now also contains some sulphide of an alkali metal, for mercury (which may be present, as its sulphide is soluble in sodium sulphide) and for metals of the sixth group, mix with a sufficient quantity of water, then with dilute $H_2 S O_4$ to acid reaction, and if the fluid does not smell strongly of $H_2 S$, add some more of the latter reagent. **163**

* You must, of course, avoid adding solution of $H_2 S$, or conducting the gas into the fluid, until the mixture smells of the reagent, *i.e.*, until the Na O H has been converted into Na S H, since this might lead to the precipitation also of the alumina which may be present in the alkaline solution, and even of sulphides of metals of the sixth group—a precipitation which is not intended here.

aa. No precipitate is formed. Absence of mercury and metals of the sixth group. Pass on to **164.**

bb. A precipitate is formed. Filter, wash the precipitate, then examine it for mercury and the metals of the sixth group according to § 184.

γ. The fluid, acidified with H_2SO_4, may still **164** contain those metals which form compound cyanogen radicals (iron, cobalt, manganese, chromium), and, besides these, also aluminium. You have to test it also for cyanogen, ferrocyanogen, cobalticyanogen, etc., and for other acids. Divide it therefore into two parts, *aa* and *bb*.

aa. Treat it according to § 192, or, as the case may be, § 193, to detect the acids.* (Cobalticyanogen may be recognized by giving a greenish precipitate with Ni salts and white precipitates with Zn and Mn salts, which may be proved to contain cobalt by means of the borax bead.)

bb. Evaporate it nearly to dryness, add some pure concentrated H_2SO_4, and heat till the free acid is for the most part expelled. Dissolve the residue in water, and test the solution for iron, manganese, cobalt, aluminium, and chromium, according to § 187.

2. Decompose another portion by continued heating with pure concentrated H_2SO_4, remove all other bases and then test for alkali metals.

II. Analysis of Silicates.

§ 198.

Whether the substance is a silicate or contains one, is **165** ascertained by the preliminary blowpipe examination with $NaPO_3$; since in the process of fusion the bases dissolve whilst the separated silicic oxide floats about in the liquid bead as a translucent swollen mass (§ 150, 8).

The analysis of silicates differs from the usual course

* It must be remembered that ferricyanogen may have been converted into ferrocyanogen thus: $K_6Fe_2(CN)_{12} + 2(FeCl_2) + 2(KOH) + H_2O = 2[K_4Fe(CN)_6] + Fe_2O_3 + 4HCl$.

in the preparatory treatment required to separate the silicic acid from the bases, and to obtain the latter in solution.

The silicates are divided into two classes, which require different methods of analysis: viz., (1) silicates readily decomposable by acids (HCl, HNO_3, H_2SO_4), and (2) silicates which are not, or only with difficulty, decomposed by acids. Many rocks consist of mixtures of the two classes.

To ascertain to which class a given silicate belongs, reduce it to a very fine powder, and digest a portion with HCl at a temperature near the boiling point. If this fails to decompose it, try another portion by long continued heating with a mixture of three parts of concentrated H_2SO_4 and one part of water. If this also fails, the silicate belongs to the second class. Whether decomposition has been effected by the acid or not, may generally be learned from external indications, as a colored solution forms almost invariably, and the separated gelatinous, flocculent, or finely pulverulent silicic acid takes the place of the original heavy powder, which grated under the glass rod with which it was stirred. But whether the decomposition is complete, or extends only to one of the components of the rock, may be ascertained by boiling the separated silicic acid, after washing, in a solution of Na_2CO_3. If perfect solution ensues, complete decomposition has been effected; if not, the decomposition is only partial. The results of these preliminary tests will show whether the silicate should be examined according to § 199, or § 200, or § 201.

Before proceeding further, examine a portion of the substance also for *water*, by heating it in a glass tube. If the substance contains hygroscopic moisture,* it must first be dried at 100° for a long time. Apply a gentle heat at first, but ultimately an intense heat; you may also conveniently combine with this a preliminary examination for *fluorine* (§ 146, 8).

* [In some cases it is impossible to distinguish between constitutional and hygroscopic water; in other cases, combined water certainly escapes at 100°.—Ed.]

A. Silicates decomposable by Acids.

§ 199.

*a. Silicates decomposable by hydrochloric or nitric acid.**

166 1. Digest the finely pulverized silicate with H Cl or $H N O_3$ at a temperature near the boiling point, until complete decomposition is effected, filter off a small portion of the fluid, evaporate the remainder, together with the silicic acid suspended therein, to dryness, heat the residue at 100° (scarcely above), with constant stirring, until hardly any more acid fumes escape, allow to cool, moisten with H Cl, or, as the case may be, with $H N O_3$, afterwards add a little water, and heat gently for some time.

This operation effects the separation of the SILICIC ACID, and the solution of the bases in the form of chlorides or nitrates. Filter, wash the residue thoroughly, and examine the solution by the usual method, beginning at § 182, II. or III. The residual silicic acid must always be tested, as it cannot under any circumstances be considered pure. It frequently contains Ti, occasionally Ba and possibly Sr as sulphates and often a little Al. It is best tested by repeated heating in a platinum dish with H F and $H_2 S O_4$, until all the silicic acid is removed in form of $Si F_4$. The residue is ignited, fused with sodium disulphate, and then treated with cold water. If anything insoluble now remains, it is filtered off and tested according to § 99 for BARIUM and STRONTIUM SULPHATES. The dilute aqueous solution is tested by long boiling for TITANIUM† (§ 104, 9), and the filtrate therefrom is tested by $N H_4 O H$ for ALUMINIUM. (Should there be any chance of the presence of Ag Cl in the silicic acid, digest a por-

* $H N O_3$ is preferable to H Cl where Ag or Pb compounds are present.

† If the silicic acid has been separated by evaporation on the water bath, only a small part of the titanic acid will be found remaining with it; the rest will pass into the H Cl solution, and will be precipitated by $N H_4 O H$ in conjunction with Fe and Al. To find this, fuse the dried precipitate with sodium disulphate, dissolve the fusion in cold water, filter if necessary, dilute considerably, pass $H_2 S$ until all iron is reduced to the ferrous state, and (without filtering off the S) keep the fluid boiling for half an hour with a constant current of $C O_2$ passing through it. Filter, wash, and ignite; the S will burn off, titanic oxide will remain. Should it still contain Fe, redissolve it by fusion with sodium disulphate and treatment with cold water, and precipitate by boiling with sodium thiosulphate.

tion with NH_4OH, filter, and examine the filtrate by supersaturation with HNO_3.)

2. As in silicates, and more particularly in those de- 167
composed by H Cl, there are often found other acids, as well as metalloids, the following instructions must be attended to, that none of these substances may be overlooked:

α. CARBONATES are detected in treating with H Cl. SULPHIDES are often detected in the same operation, otherwise they may be tested for according to § 156, 8.

β. If the separated silicic acid is black, and turns white upon ignition in the air, this indicates the presence of CARBON or of ORGANIC SUBSTANCES. In presence of the latter, the silicates emit an empyreumatic odor upon being heated in the glass tube.

γ. Test the portion of the H Cl solution filtered off before evaporating, for SULPHURIC ACID, PHOSPHORIC ACID and ARSENIC ACID—for sulphuric acid by diluting and adding $BaCl_2$; for arsenic acid by heating the solution to 70° and conducting H_2S into it; for phosphoric acid by adding HNO_3, evaporating to dryness on the water bath, warming the residue with HNO_3, filtering, and adding molybdic solution. Where arsenic is found, phosphoric acid is tested for in the fluid filtered from As_2S_3.

δ. BORIC ACID is best detected by fusing a portion 168
of the substance in a platinum spoon with Na_2CO_3, boiling the fused mass with water, and testing the solution by § 144, 6.

ε. With many silicates, boiling with water is sufficient to dissolve the CHLORIDES present, which may then be readily detected in the filtrate by $AgNO_3$; the safest way, however, is to dissolve the mineral in dilute HNO_3, and test the solution with $AgNO_3$.

ζ. FLUORIDES, which often occur in silicates in greater or smaller proportion, may be detected by § 116, 6.

b. Silicates which resist the action of hydrochloric acid, but are decomposed by concentrated sulphuric acid.

Heat the finely pulverized mineral with a mixture of 3 parts of concentrated pure $H_2 S O_4$ and 1 part of water (best in a platinum dish), finally drive off the greater portion of the acid, boil the residue with H Cl, dilute, filter, and treat the filtrate as directed § 183, and the residue, which, besides the separated silicic acid, may contain also sulphates of the alkali-earth metals, etc., as directed § 199, 1. If you wish to examine silicates of this class for acids and acid radicals, treat a separate portion of the substance according to § 200. 169

B. SILICATES WHICH ARE NOT DECOMPOSED BY ACIDS.*

§ 200.

As the silicates of this class are most conveniently decomposed by fusion with $Na_2 C O_3$, the portion so treated cannot, of course, be examined for alkali metals. The analytical process is therefore divided into two principal parts, a portion of the mineral being examined for the silicic acid and the bases, with the exception of the alkalies, whilst another portion is specially examined for the latter. The mineral must also be examined for other acids. 170

1. *Detection of the silicic acid and the bases, with the exception of the alkalies.*

Reduce the mineral to a very fine powder, mix this with 4 parts of $Na_2 C O_3$, and heat the mixture in a platinum crucible until the mass is in a state of calm fusion. Place the red-hot crucible on a thick cold iron plate, and let it cool there: this will generally enable you to remove the fused cake from the crucible, in which case break the mass to pieces, and keep a portion for the examination for acids. Put the remainder, or, if the mass still adheres to the crucible, the latter with its contents into a porcelain dish, pour on water, add H Cl, and warm it until the mass is dissolved, with the exception of the 171

* It will be understood, from what has been stated § 198, that these are not decomposed by heating with H Cl and $H_2 S O_4$ in open vessels; but by heating them, reduced to a fine powder, in a sealed glass tube, with a mixture of 3 parts of concentrated $H_2 S O_4$ and 1 part of water, or with H Cl to 200°-210°, most of them are decomposed, and may accordingly be analyzed also in this manner (AL. MITSCHERLICH).

silicic acid. Evaporate to dryness, and treat the residue as directed, **166.**

2. *Detection of the alkalies.*

To effect this the silicate must be decomposed by **172** means of a substance free from alkalies. The following methods are the most suitable:

[*a.* DECOMPOSITION BY MEANS OF CALCIUM CARBONATE AND AMMONIUM CHLORIDE. Mix 1 part of the pulverized substance with 6 parts of precipitated $CaCO_3$, and $\frac{1}{2}$ part of pulverized NH_4Cl, place in a platinum crucible and heat to bright redness for 30 to 40 minutes. The crucible, with its contents (which should be in a coherent, sintered, but not thoroughly fused condition), is placed in a beaker, covered with water and heated to near the boiling point for half an hour. The whole is then brought upon a filter, the filtrate, containing the alkali metal and calcium hydroxides and calcium chloride, is treated with a little NH_4OH and with $(NH_4)_2CO_3$ in slight excess, and heated to boiling, filtered, and the filtrate evaporated to dryness and gently ignited to expel ammonium salts. The residue is dissolved in a little water, one or two drops of $(NH_4)_2CO_3$, and a drop of $(NH_4)_2C_2O_4$, added, the mixture is heated, filtered, the filtrate is evaporated to dryness, ignited, and the residual alkali-metal chlorides examined according to § 190. (*J. L. Smith.*)—EDITOR.]

b. DECOMPOSITION WITH A FLUORIDE. Mix the finely **173** powdered substance with 5 parts of powdered fluor spar, and then (in a platinum crucible) with enough concentrated H_2SO_4 to make a thin paste, warm gently for some time (where the fumes will pass off in a good draught), and finally heat more strongly until the excess of H_2SO_4 is expelled. Boil the residue with water, add $BaCl_2$ cautiously as long as it produces a precipitate, then $Ba(OH)_2$ to alkaline reaction, boil, filter, treat with $(NH_4)_2CO_3$ and NH_4OH as long as anything is precipitated, filter, evaporate, ignite, and proceed further as directed, § 190.

3. *Examination for fluorine, chlorine, boric acid, phosphoric acid, arsenic acid, and sulphuric acid.*

Use for this purpose the portion of the fused mass re- 174
served in 171, or, if necessary, fuse a separate portion of the finely pulverized substance with 4 parts of pure $Na_2 C O_3$ until the mass flows calmly; boil the fused mass with water, filter the solution, which contains all the fluorine as Na F, all the chlorine as Na Cl, all the boric acid as borate, all the sulphuric acid as sulphate, all the arsenic acid as arsenate, and at least part of the phosphoric acid as phosphate of sodium, and treat as follows:

a. Acidify a small portion with $H N O_3$, and test for CHLORINE with $Ag N O_3$.

b. Test another portion for BORIC ACID as directed § 144, 6.

c. To detect FLUORINE, treat a third portion as directed § 146, 7.

d. Acidify the remainder with H Cl and test a small portion with $Ba Cl_2$ for SULPHURIC ACID; heat the remainder to 70°, and test with $H_2 S$ for ARSENIC ACID. If no precipitate forms, evaporate the fluid, if a precipitate forms, the filtrate, with addition of $H N O_3$ to dryness, treat the residue with $H N O_3$ and water, and examine the solution for PHOSPHORIC ACID with magnesium mixture, or with molybdic solution (§ 142).

C. SILICATES WHICH ARE PARTIALLY DECOMPOSED BY ACIDS.

§ 201.

Most rocks are mixtures of several silicates, of which 175
some are often decomposable by acids, others not. If such substances were analyzed by the same method as the absolutely insoluble silicates, the analyst would indeed detect all the elements present, but the analysis would afford no satisfactory insight into the actual composition of the mineral.

It is therefore advisable to examine separately those constituents which show a different deportment with

acids. For this purpose digest the very finely pulverized substance for some time with H Cl at a gentle heat, filter off a small portion of the solution, evaporate the remainder with the residue to dryness, heat the residue at 100° (scarcely above), with stirring, until no more, or very little acid vapor is evolved, allow to cool, moisten with H Cl, heat gently with water, and filter.

The filtrate contains the bases of that part of the mixed mineral which has been decomposed by H Cl; examine this as directed **166.** Examine the portion first filtered off as directed **167**, γ. Test portions of the original substance for other acids as directed **167**, α and β, and **168.** Boil the residue—which, besides the silicic acid separated from the decomposed portion of the silicate, contains that part of the mixed mineral which has resisted the action of H Cl—with an excess of solution of Na_2CO_3, filter hot, and wash, first with hot solution of Na_2CO_3, finally with boiling water. Treat the residuary undecomposed part of the mineral, thus freed from the admixed separated silicic acid, according to § 200. Acidify the alkaline filtrate with H Cl, evaporate to dryness, treat with H Cl and water, filter off the silicic acid, render the filtrate alkaline with ammonia, and warm; the precipitate thus formed (if any) is to be treated with the separated silicic acid according to **166**, in order to detect titanic acid. In cases where it is of no interest to effect the separation of the silicic acid of the part decomposed by acids, you may omit the troublesome operation with Na_2CO_3, and may proceed at once to the decomposition of the residue.

III. Analysis of Natural Waters.

§ 202.

In the examination of natural waters the analytical **176** process is simplified by the circumstance that we know from experience what substances are usually present. Now, although a quantitative analysis alone can properly inform us of the true character of a water, since the differences between waters are principally caused by the

different proportions of the constituents, still a qualitative analysis may render very good service, especially if the analyst notes whether a reagent produces a faint or a distinctly marked turbidity, a slight or a copious precipitate; since these circumstances will enable him to make an approximate estimate of the relative proportions of the constituents.

I separate here the analysis of ordinary drinking waters from that of mineral waters, in which latter we may also also include sea water; for although no well-defined line can be drawn between the two classes, still the analytical examination of the former is necessarily by far the simpler, as the number of substances to be looked for is much more limited.

A. Analysis of Potable Waters (Spring Water, Well Water, River Water, etc.).

§ 203.

We know from experience that the substances to be 177
had regard to in the analysis of such waters are the following:

a. Metals: Potassium, sodium, ammonium, calcium, magnesium, iron.

b. Acids, etc.: Sulphuric acid, phosphoric acid, silicic acid, carbonic acid, nitric acid, nitrous acid, chlorine.

c. Organic matter.

d. Mechanically suspended substances: Clay, etc.

Potable waters contain indeed also other constituents besides those enumerated here, as may be inferred from the origin and formation of springs, etc., and as has, moreover, been fully established by the results of analytical investigations;* but the quantity of such constituents is so trifling that they commonly escape detection, unless many pounds of the water are subjected to the

* Chatin (Journ. de Pharm. et de Chim. (3), 27, 418) found iodine in all fresh-water plants, but not in land plants, a proof that the water of rivers, brooks, ponds, etc., contains traces, even though extremely minute, of metallic iodates or iodides. According to Marchand (Comp. Rend., 31, 495), all natural waters contain iodine, bromine, and lithium. Van Anken has demonstrated the presence of iodine in almost all the potable waters of Holland. And it may be affirmed with the same certainty that all, or at all events most, natural waters contain compounds of strontium, barium, fluorine, etc.

analytical process. I therefore omit here the mode of their detection (see § 204).

1. Boil 1,000 to 2,000 grm. of the carefully collected **178** water in a porcelain dish to one-half. (Glass vessels are to be avoided, as boiling water attacks them much more than porcelain.) This generally produces a precipitate. Pass the fluid through a perfectly clean filter (free from iron and lime), wash the precipitate well, after having removed the filtrate, then examine both as follows:

a. Examination of the precipitate.

The precipitate contains those constituents of the **179** water which were only kept in solution through the agency of free carbonic acid, or, as the case may be, in the form of bicarbonates, viz., calcium carbonate, magnesium carbonate, ferric hydroxide (which precipitates upon boiling a solution containing ferrous bicarbonate), also ferric silicate, and in presence of phosphoric acid, ferric phosphate; calcium phosphate; also silicic acid, sometimes calcium sulphate (if that substance is present in large proportion) and clay which was mechanically suspended in the water.

Dissolve the precipitate on the filter in the least possible quantity of dilute H Cl (effervescence indicates CARBONIC ACID), and treat separate portions of the solution as follows:

α. Add K C N S, or K_4 Fe (C N)$_6$ drop by drop, to test for IRON.

β. Boil, add N H_4 O H, filter if necessary, mix **180** the filtrate with excess of $(N H_4)_2 C_2 O_4$, and let the mixture stand for some time in a warm place. A white precipitate indicates CALCIUM (in the form of carbonate, or also in that of sulphate if sulphuric acid is detected in *γ*). Filter, mix the filtrate again with N H_4 O H, add some Na_2 H P O_4, stir with a glass rod, and let the mixture stand for twelve hours. A white crystalline precipitate, which is often visible only on the sides of the vessel when the fluid is poured out, indicates MAGNESIUM (as carbonate).

γ. Add Ba Cl_2, and let the mixture stand for

twelve hours in a warm place. A precipitate indicates SULPHURIC ACID. If very small it is best seen by cautiously decanting the supernatant clear fluid and shaking the small remaining quantity about in the glass.

δ. Evaporate with addition of HNO_3 to dry- 181
ness, treat the residue with HNO_3 and water, filter off any SILICIC ACID, and test the filtrate for PHOSPHORIC ACID with molybdic solution (§ 142, 10), or with sodium acetate and Fe_2Cl_6 (§ 142, 9).

b. Examination of the filtrate.

α. Mix a portion with a little HCl and $BaCl_2$. 182
A white precipitate, which makes its appearance at once, or perhaps only after standing some time, indicates SULPHURIC ACID.

β. Mix a portion with HNO_3 and add $AgNO_3$. A white precipitate or turbidity indicates CHLORINE.

γ. Test a portion for PHOSPHORIC ACID, by evaporating with HNO_3, taking up with the same and proceeding as in **181.**

δ. Evaporate a large portion until highly concentrated, and test the reaction of the fluid. If it is alkaline, if a drop of the concentrated clear solution effervesces when mixed on a watch-glass with a drop of acid, and if calcium carbonate precipitates on the cautious addition of calcium chloride to the alkaline fluid, then CARBONATE OF AN ALKALI METAL is present. Should this be the case, evaporate the fluid to perfect dryness, boil the residue with alcohol, filter, evaporate the solution to dryness, dissolve the residue in a little water, and test the solution for NITRIC ACID, as directed § 159, 7, 8 or 9.*

ε. Mix the remainder of the filtrate with NH_4Cl, NH_4OH, and excess of $(NH_4)_2C_2O_4$, and let the mixture stand some time. A precipitate indicates CALCIUM. Filter, and—

* The nitric acid may often be found without trouble, by evaporating the water to a small residue, and testing this at once for it.

aa. Test a small portion with NH_4OH and Na_2HPO_4 for MAGNESIUM.

bb. Evaporate the remainder to dryness, ignite, remove the magnesium which may be present (112), and test for POTASSIUM and SODIUM, according to § 190.

2. Acidify a tolerably large portion of the filtered water with pure HCl, and evaporate nearly to dryness; divide the residue into two parts, *a* and *b*. 183

a. Test with $Ca(OH)_2$ for AMMONIUM (§ 91, 3).*

b. Evaporate to dryness, moisten the residue with HCl, add water, warm, and filter if a residue remains. The residue may consist of SILICIC ACID and, if the water has not been filtered quite clear, also of CLAY; these two substances may be separated by boiling with solution of Na_2CO_3. The residue is often dark-colored from the presence of organic substances; but it becomes perfectly white upon ignition.

3. Mix another portion of the water, freshly taken, with lime water. If a precipitate is produced, FREE CARBONIC ACID or BICARBONATES are present. If free carbonic acid is present, no permanent precipitate is obtained when a large portion of the water is mixed with only a small amount of lime water, since in that case soluble calcium bicarbonate is formed. 184

4. Test for NITROUS ACID,† by mixing a portion of the water with some KI and starch paste made of 1 part of the purest KI, 20 parts of starch, and 500 parts of water) and pure dilute H_2SO_4, and observe whether a blue coloration makes its appearance, either at once or at least after a few minutes (§ 158, 1). The reagents should be tested by making a counter-experiment with pure water. 185

5. ORGANIC MATTER is detected by the blackening which occurs when a portion of the water is evaporated to dryness and gently ignited. If this experiment is to give 186

* In clear water ammonia may be tested for quite satisfactorily without evaporating either by means of $HgCl_2$ with K_2CO_3 or by NESSLER's test (§ 92).

† SCHÖNBEIN found this acid in rain and snow water.

conclusive results, the evaporation as well as the ignition must be conducted in a flask or retort.

6. FETID SUBSTANCES (decaying organic matter) are detected best by filling a bottle two-thirds with the water, covering it with the hand, shaking, and smelling. If the smell is of H_2S, proceed as directed § 205, 3. Whether there are other smelling organic matters present besides, may be ascertained by adding a little $CuSO_4$ to the water, before smelling it.

7. If you wish to examine the MATTERS MECHANICALLY SUSPENDED in a water (in muddy river-water, for instance), fill a large glass bottle with the water, cork securely, and let it stand at rest for several days, until the suspended matter has subsided; remove now the clear fluid with the aid of a siphon, filter the remainder, and examine the sediment remaining on the filter. As this sediment may consist of the finest dust of various minerals, treat it first with dilute HCl, then examine the part insoluble in that menstruum as directed § 198. 187

8. As LEAD may be present, arising from leaden pipes, treat a large quantity with H_2S, allow to stand for some time, and should a black precipitate form, examine this as directed § 186. To detect very minute traces of lead, acidify 6 or 8 litres of the water with acetic acid, add a little ammonium acetate, to prevent the lead precipitating as sulphate, evaporate to a small residue, filter, conduct H_2S into the filtrate, and examine a black precipitate which may form by § 186.

B. ANALYSIS OF MINERAL WATERS.

§ 204.

The analysis of mineral waters embraces a larger number of constituents than that of potable water. The following are the principal of the additional bodies to be looked for: 188

CÆSIUM, RUBIDIUM, THALLIUM, LITHIUM, BARIUM, STRONTIUM, ALUMINIUM, MANGANESE, BROMINE, IODINE, FLUORINE, BORIC ACID, HYDROSULPHURIC ACID (thiosulphuric or hypo-

sulphurous acid),* CRENIC ACID and APOCRENIC ACID (formic acid, propionic acid, etc., nitrogen gas, oxygen gas, methane).*

The analyst has moreover to examine the muddy ochreous or hard sinter deposits of the spring, or also the residue left upon the evaporation of very large quantities of water, for ARSENIC, ANTIMONY, COPPER, LEAD, COBALT, NICKEL, and other heavy metals. The greatest care is required in this examination, to ascertain whether these metals come really from the water, and do not perhaps proceed from pipes, stopcocks, etc. The absolute purity of the reagents employed in these delicate investigations must also be ascertained with the greatest care.

1. EXAMINATION OF THE WATER.

a. OPERATIONS AT THE SPRING.

§ 205.

1. Filter the water, if not perfectly clear, through washed filter paper, into large bottles with glass stoppers. The sediment remaining on the filter, which possibly contains, besides the flocculent matter suspended in the water, also those constituents which separate at once upon coming in contact with the air (ferric hydroxide and ferric phosphate, silicate, and arsenate), is taken to the laboratory, to be examined afterwards according to § 207. **189**

2. The presence of FREE CARBONIC ACID is usually sufficiently evident to the eye. However, to convince yourself by positive reactions, test the water with fresh prepared solution of litmus, and with lime water. If carbonic acid is present, the former acquires a wine-red color; the latter produces turbidity, which must disappear again upon addition of the mineral water in excess. **190**

3. Free HYDROSULPHURIC ACID is most readily detected by the smell. For this purpose half fill a bottle with the mineral water, cover with the hand, shake, and smell the **191**

* Respecting the constituents in brackets, I refer to the corresponding chapter in my Quantitative Analysis, as the detection of these matters generally comprises also their quantitative estimation.

bottle. In this way distinct traces of hydrosulphuric acid are often found which would escape detection by reagents. However, if you wish to have some visible reactions, fill a large white bottle with the water, add a few drops of solution of lead acetate in soda, place the bottle on a white surface, and look in at the top, to see whether the water acquires a brownish color or deposits a blackish precipitate;—or half fill a large bottle with water, and close with a cork to which is attached a slip of paper previously saturated with solution of lead acetate and then moistened with ammonium carbonate; shake the bottle gently from time to time, and observe whether the paper acquires a brownish tint in the course of a few hours. If the addition of the lead acetate has produced a brown color, or precipitate, whilst the test with the paper gives no result, this indicates that the water contains an alkaline sulphide, but no free hydrosulphuric acid.

4. Mix a wineglassful of the water with some tannic 192
acid, another wineglassful with some gallic acid. If the former imparts a red-violet, the latter a blue-violet color, FERROUS COMPOUNDS are present. Instead of the two acids, you may employ infusion of galls, which contains them both. The colorations make their appearance only after some time, and increase in intensity from the top—where the air acts on the fluid—towards the bottom of the vessel.

5. Test for NITROUS ACID and FETID ORGANIC SUBSTANCES 193
according to **185** and **186**. If the water contains hydrosulphuric acid, remove it before testing for nitrous acid by very cautious addition of silver sulphate (no silver salt must under any circumstances remain in the solution).

b. Operations in the Laboratory.

§ 206.

As it is always desirable to obtain, even in the qualitative examination, some information as to the proportions in which the several constituents are present, it is advisable to analyze a comparatively small portion for the principal constituents, and to ascertain, as far as may

be practicable, the relative proportions in which these constituents exist, and thus to determine the character of the water; then to examine a far larger portion for the constituents which are present in small quantity; and finally a very large portion of the sinter for those constituents which are present merely in traces. For this purpose proceed as follows:

1. EXAMINATION FOR THOSE CONSTITUENTS WHICH ARE PRESENT IN LARGE QUANTITIES.

194 *a.* Boil about 3 lbs. of the clear water, or of the water filtered at the spring, in a porcelain dish (a flask is less suitable) for one hour, taking care, however, to add from time to time some distilled water, that the quantity of liquid may remain undiminished, and thus that only those salts may be separated which owe their solution to the presence of carbonic acid. Filter and examine the precipitate and the filtrate as directed § 203.

b. Test for AMMONIUM, SILICIC ACID, ORGANIC MATTERS, etc., by the methods given in § 203.

2. EXAMINATION FOR THOSE FIXED CONSTITUENTS WHICH ARE PRESENT IN MINUTE QUANTITIES.

195 Evaporate a large quantity (at least 20 lbs.) of the water in a silver or porcelain dish to dryness; conduct this operation with the most scrupulous cleanliness in a place as free as possible from dust. If the water contains no alkali carbonate, add pure $K_2 C O_3$ in slight excess. The process of evaporation may be conducted at first over a gas lamp, but ultimately the sand bath must be employed. Heat the dry mass to very faint redness; if in a silver dish, you may at once proceed to ignite it; but if you have it in a porcelain dish, first transfer it to a silver or platinum vessel before proceeding to ignition. If the mass turns black in this process, ORGANIC MATTERS may be assumed to be present.*

* This inference is, however, correct only if the water has been effectually protected from dust during evaporation; if this has not been the case, and you yet wish to ascertain beyond doubt whether organic matters are present, evaporate a separate portion of the water in a retort. If you find organic matter, and wish to know whether it consists of crenic acid or of apocrenic acid, treat a portion of the residue as directed § 207, 3.

Mix the residue thoroughly, and divide it into 3 portions, *a* and *b* being each about a quarter, and *c* one-half.

a. EXAMINATION FOR PHOSPHORIC ACID.

Warm the portion *a* with water, add pure H N O_3 196
in sufficient excess, evaporate on the water bath to dryness, warm the residue with H N O_3 dilute slightly, filter through paper washed with H Cl, and test with molybdic solution (§ 142, 10).

b. EXAMINATION FOR FLUORINE.

Heat the portion *b* with water, add Ca Cl_2 as long 197
a precipitate continues to form, let deposit and collect the precipitate, which consists chiefly of calcium and magnesium carbonates, on a filter. Wash, dry, ignite, treat with water in a small dish, add acetic acid in slight excess, evaporate on the water bath to dryness, keeping the dish on the bath until all smell of acetic acid has disappeared, add water, heat, filter off the solution of the acetates of the alkali-earth metals, wash, dry or ignite the residue, and test it as directed § 146, 5.

c. EXAMINATION FOR THE REMAINING FIXED CONSTITUENTS PRESENT IN MINUTE QUANTITIES.

Boil the portion *c* repeatedly with water, filter, 198
and wash the undissolved residue with boiling water. You have now a residue (α), and a solution (β).

α. The *residue* consists chiefly of calcium carbonate, magnesium carbonate, silicic acid, and—in the case of chalybeate springs—ferric hydroxide. But it may contain also minute quantities of BARIUM, STRONTIUM, ALUMINIUM, MANGANESE, and TITANIUM, and must accordingly be examined for these substances.

Treat it with water in a platinum or porcelain dish, add H Cl to slightly acid reaction, then 4 or 5 drops of dilute H_2SO_4, evaporate on the water bath to dryness, moisten with a small quantity of H Cl, then add water, warm gently, filter, and wash.

aa. EXAMINATION OF THE RESIDUE INSOLUBLE IN 199
HYDROCHLORIC ACID. This will mostly consist of silicic acid; but it may contain also sulphates of

the alkali-earth metals, titanic acid, and carbon. Heat it in a platinum dish repeatedly with H F or NH_4F with addition of H_2SO_4, till all silicic acid is expelled. Finally evaporate to dryness, fuse the residue (if any) with potassium disulphate, treat the fusion with cold water, filter and test the solution for TITANIC ACID by protracted boiling. If there was a residue on treating the fusion with water, wash it and incinerate the filter. When a spectroscope is at disposal, take up the ash on the loop of a platinum wire, expose for some time to the reducing flame, moisten with H Cl, and examine for BARIUM. Strontium will not be found here except perhaps in traces. When a spectroscope is not at hand, set aside the ash for subsequent examination.

bb. EXAMINATION OF THE HYDROCHLORIC ACID SO- 200
LUTION. Mix in a flask with pure NH_4Cl, add NH_4OH until the fluid is just alkaline, then $(NH_4)_2S$ free from NH_4OH; close the flask, filled to the neck, and let it stand for 24 hours in a moderately warm place. If a precipitate has formed at the end of that time, filter off, dissolve in H Cl, boil, add K O H (§ 34, *c*) in excess, boil again, filter, and test the *filtrate* for ALUMINIUM, by acidifying with H Cl, and heating with NH_4OH;* divide the *residue* into two parts, test one for MANGANESE with Na_2CO_3 before the blowpipe, the other for IRON by dissolving in H Cl and adding K C N S or $K_4Fe(CN)_6$.

The filtrate from the ammonium sulphide precipitate may contain traces of barium, and will contain all or nearly all the strontium. Add to it $(NH_4)_2CO_3$, filter alter long standing, wash the precipitate dry, subject it to ENGELBACH'S process (end of § 99), and treat the aqueous extract of the ignited precipitate as follows: If a spectroscope is at command, evaporate it

* There is no use in testing for aluminium unless the evaporation has been effected in a platinum or silver dish.

to dryness with H Cl and examine the residue in the instrument. If a spectroscope is not at command, evaporate it nearly to dryness with $(NH_4)_2SO_4$, boil with a saturated solution of $(NH_4)_2SO_4$, filter, wash the precipitate, dry, incinerate, add the residue set aside in **199**, fuse with Na_2CO_3, treat with water, wash, dissolve the residue in H Cl, and test the solution according to § 99.

β. The *alkaline solution* contains the salts of the **201** alkali metals, and usually also magnesium and traces of calcium. You have to examine it now for NITRIC ACID,* BORIC ACID, IODINE, BROMINE and LITHIUM. Evaporate until very concentrated, let it cool, and place the dish in a slanting position, that the small quantity of liquid may separate from the saline mass; transfer a few drops of the concentrated solution to a watch-glass by means of a glass rod, just acidify with H Cl, and test with turmeric paper for BORIC ACID. Evaporate the whole contents of the dish, with stirring, to perfect dryness, and divide the residuary powder into two portions, *aa* being about two-thirds, and *bb* one-third.

aa. EXAMINE THE LARGER PORTION FOR NITRIC **202** ACID, IODINE AND BROMINE.

Put the powder into a flask, add alcohol of 90 per cent., boil in the water bath, and filter hot; repeat the same operation a second and a third time. Mix the alcoholic extract with a few drops of potassa, distil almost all the spirit off, and allow to cool. If minute crystals separate, these may consist of potassium nitrate; pour off the fluid, wash the crystals with some spirit; dissolve in a very little water, and test the solution for NITRIC ACID, with indigo, or with brucin, or with potassium iodide, starch paste and zinc (§ 159). Evaporate the alcoholic solution now

* The nitric acid originally present may have been destroyed by the ignition of the residue in **195** if the latter contained organic matter. If you have reason to fear that such has been the case, and you have not already found nitric acid in **194**, examine a larger portion of non-ignited residue for that acid, according to the directions of **202**.

to dryness. If you have not yet found nitric acid, dissolve a small portion of the residue in a very little water, and examine the solution for that acid. Treat the remainder or, as the case may be, the whole of the residue three times with warm alcohol, filter, evaporate the filtrate to dryness with addition of a drop of K O H, dissolve the residue in a very little water, acidify slightly with $H_2 S O_4$, add some pure $C S_2$, and test for IODINE * with K N O_2, or a drop of solution of $N_2 O_4$ in $H_2 S O_4$. After having carefully observed the reaction, test the same fluid for BROMINE with Cl water according to § 157.

bb. EXAMINE THE SMALLER PORTION FOR LITHIUM. 203

Warm the smaller portion of the residue (which, if lithium is present, must contain that metal as carbonate or phosphate) with water, add H Cl to distinctly acid reaction, evaporate *nearly* to dryness, then mix with pure alcohol of 90 per cent., which will separate the greater portion of the Na Cl, and dissolve all the lithium salt. Drive off the alcohol by evaporation, and, if you have a spectroscope, examine the residue with this for LITHIUM (§ 93, 3). If you have no spectroscope, dissolve the residue in water and a few drops of H Cl, add a little $Fe_2 Cl_6$, then N H_4 O H in *slight* excess, and a small quantity of $(N H_4)_2 C_2 O_4$; let the mixture stand for some time, then filter off the fluid, which is now entirely free from phosphoric acid and calcium; evaporate the filtrate to dryness, and gently ignite until the N H_4 salts are expelled; treat the residue with some Cl water (to remove I and Br) and a few drops of H Cl, and evaporate to dryness; add a little water and (to remove Mg) some finely divided Hg O,

* [According to SONSTADT (*Chem. News*, XXV., pp. 196, 231 and 241), sea water contains iodine in the form of *iodates*, which do not give the usual reactions for iodine until treated with reducing agents. To test for iodine in sea water, directly, Sonstadt advises to add to 50 or 100 c.c. of the water a few drops of *pure* H Cl, a bit of magnesium metal, and to shake up with a few drops of $C S_2$. The latter acquires a purple tinge after a few minutes.—ED.]

evaporate to dryness, and gently ignite until the HgO is just driven off; add a drop of HCl, treat with a mixture of absolute alcohol and anhydrous ether, filter, concentrate the filtrate by evaporation, and set fire to the alcohol. If it burns with a carmine flame LITHIUM is present. By way of confirmation convert the lithium found into phosphate (§ 93, 3).

3. EXAMINATION FOR THOSE CONSTITUENTS WHICH ARE PRESENT IN MOST MINUTE QUANTITIES.

204 Evaporate 200 or 300 lbs. of the water in a large, perfectly clean iron vessel until the salts soluble in water begin to separate. If the mineral water contains no Na_2CO_3, add sufficient of that substance to render the fluid distinctly alkaline. After evaporation filter the solution off, wash the precipitate, without adding the washings to the first filtrate, and

a. Examine the *precipitate* by the method given § 207 for sinter deposits:

b. Mix the *solution* with HCl, to acid reaction, heat, just precipitate the H_2SO_4 which may be present with $BaCl_2$, filter, evaporate the filtrate to dryness, digest the residue with alcohol of 90 per cent., and examine the solution for CÆSIUM and RUBIDIUM according to § 93, at the end. Treat the residue insoluble in alcohol as follows: Make a hot concentrated solution of it in water, add NH_4OH in excess, filter if necessary, add KI while still hot, and allow to stand. If a precipitate forms, test it for THALLIUM in the spectroscope.

II. EXAMINATION OF THE SINTER DEPOSIT.

§ 207.

205 1. Free the deposit from impurities, by picking, sifting, elutriation, etc., and from the soluble salts adhering to it, by washing with water; digest a large quantity (about 200 grammes) with water and HCl (effervescence: CARBONIC ACID) at a very moderate heat until the soluble

part is completely dissolved; dilute, let cool, filter, and wash the residue.

a. Examination of the filtrate.

α. Heat the larger portion to 70°, pass H_2S for some time and also during the cooling. Allow to stand in a moderately warm place till the smell of the gas is almost gone, and filter. **206**

Wash and dry the precipitate, remove the greater part of the free sulphur by digesting and washing with CS_2, warm gently with yellow potassium sulphide, dilute, filter, wash with water containing potassium sulphide, and precipitate the filtrate and washings with HCl. Allow the precipitate to settle, filter it off, wash, dry, extract again with CS_2, treat the residue (if any) together with the filter in a small porcelain dish with pure red fuming nitric acid, warm till the greater part of the acid is expelled, add excess of Na_2CO_3, then a little $NaNO_3$, fuse, treat the fusion with cold water, filter, wash with diluted alcohol, and test the aqueous solution for ARSENIC by **65** and **66**, the residue for ANTIMONY and TIN by dissolving in dilute HCl, and treating the solution with zinc free from lead in a platinum capsule (**67**). **207**

If a residue remained on treating the H_2S precipitate with K_2S, wash, remove from the filter by a jet of water, boil with a small quantity of dilute HNO_3, filter, wash, and treat the contents of the filter first with H_2S, in order not to miss lead sulphate which may possibly be present here, then test them for BARIUM and STRONTIUM according to **199**. Mix the nitric acid solution with a little pure H_2SO_4, evaporate to dryness on a water bath and treat with water; if a residue, it consists of LEAD sulphate. To make sure, filter it off, wash, and see if it turns black with H_2S. Test the filtrate from PbSO with NH_4OH, and with $K_4Fe(CN)_6$ for COPPER. **208**

Take a portion of the filtrate from the H_2S precipitate, evaporate it to dryness with excess of HNO_3 **209**

on a water bath, treat with HNO_3 and water, filter, and test the solution for PHOSPHORIC ACID with molybdic solution. Transfer the remainder of the filtrate from the H_2S precipitate to a flask, add NH_4Cl, then NH_4OH until the fluid is just alkaline, lastly $N(H_2)S$ free from NH_4OH, fill the flask to the neck, close the mouth, allow to stand in a moderately warm place till the supernatant fluid is yellow without a shade of green, filter, and wash with water containing $(NH_4)_2S$. Treat the precipitate with dilute HCl, and proceed to test for COBALT, NICKEL, IRON, MANGANESE, ZINC, ALUMINIUM AND SILICA according to **96–104**. To examine for TITANIC ACID throw down a part of this HCl solution with NH_4OH, and treat the precipitate according to **166**. In the filtrate from the $(NH_4)_2S$ precipitate throw down the CALCIUM and STRONTIUM and any BARIUM which may be present with $(NH_4)_2CO_3$ and $(NH_4)_2C_2O_4$, and test the precipitate for the two last by ENGELBACH'S method (end of § 99). Finally test the filtrate from the calcium precipitate for MAGNESIUM.

β. Mix a portion, considerably diluted, with $BaCl_2$, and allow it to stand 12 hours in a warm place. A white precipitate indicates SULPHURIC ACID.

b. Examination of the residue.

Consists of sand, silicic acid, clay and organic matter; also sulphur (if the water contained H_2S), and sulphates of barium and strontium. Boil with a solution of Na_2CO_3 and NaOH to dissolve the SILICIC ACID and sulphur, filter, and treat on the paper with dilute HCl to dissolve barium and strontium and leave the clay and sand. Test the HCl solution according to **200** for BARIUM and STRONTIUM. **210**

2. For FLUORINE, take a separate portion of the deposit, mix with about half its weight of pure slacked lime (if $CaCO_3$ is not present in abundant quantity), ignite (blackening indicates organic matter), add water, and **211**

then acetic acid in excess, evaporate till the excess of acid is expelled, and proceed as directed **197.**

3. Boil the deposit for a considerable time with con- **212** centrated potassa, and filter.

a. Acidify a portion of the filtrate with acetic acid, add NH_4OH, allow to stand 12 hours, and then filter off the precipitate of alumina and silicic acid, which usually forms; again add acetic acid in excess, and then solution of normal cupric acetate. If a brownish precipitate is formed, this consists of cupric APOCRENATE. Mix the fluid filtered from the precipitate with $(NH_4)_2CO_3$, until the green color has changed to blue, and warm. If a bluish-green precipitate is produced, this consists of cupric CRENATE.

b. If you have detected As, use the remainder of the alkaline fluid to ascertain whether it existed as ARSENIOUS ACID or as ARSENIC ACID. (Compare § 134, 9.)

IV. Analysis of Soils.

§ 208.

Soils must contain all the constituents which are found in the plants growing upon them, with the exception of those supplied by the atmosphere and the rain. When we find, therefore, a plant, the constituents of which are known, growing in a certain soil, the mere fact of its growing there gives us some insight into the composition of that soil, and may save us, to some extent, the trouble of a qualitative analysis.

Viewed in this light, it would appear superfluous to make a qualitative analysis of soils still capable of producing plants; for it is well known that the ashes of plants contain almost invariably the same constituents, and the differences between them are caused principally by differences in the relative proportions in which the several constituents are present. But if, in the qualitative analysis of a soil, regard is had also to the proportions of the constituents, and to the state in which they are present, an analysis of the kind, if combined with an examination of the physical properties of the soil, and a

mechanical separation of its parts,* may give useful results, enabling the analyst to judge sufficiently of the condition of the soil to supersede the necessity of a quantitative analysis, which would require much time, and is a far more difficult task.

As plants can only absorb substances capable of entering into a state of solution, it is a matter of especial importance, in the qualitative analysis of a soil, to know which constituents are soluble in water;† which require an acid for their solution (in nature principally carbonic acid); and, finally, which are neither soluble in water, nor in acids, and are not, accordingly, in a position for the time being to afford nutriment to the plant. With regard to the insoluble substances, another interesting question to answer is whether they suffer disintegration readily, or slowly and with difficulty, or whether they altogether resist the action of disintegrating agencies; and also what are the products which they yield upon their disintegration.‡

In the analysis of soils, the constituents soluble in water, those soluble in acids, and insoluble constituents, must be examined separately. The examination of the organic portion also demands a separate process.

The analysis is therefore divided into the following four parts:

* With regard to the mechanical separation of the component parts of a soil, and the examination of its physical properties and chemical condition, compare F. SCHULZE, Journ. f. prakt. Chemie, 47, 241; also FRESENIUS's Quantitative Analysis, E. WOLFF, Zeitschr. f. anal. Chem. 3, 85, CALDWELL's Agricultural Chemical Analysis, and especially E. W. HILGARD, Am. Jour. Sci. III. vi. (1873), p. 288.

† It was formerly universally assumed that substances soluble in water, or in water containing carbonic acid, circulated freely in the soil so long as there existed agents for their solution; but since it has been discovered that arable soil possesses, like charcoal, the property of withdrawing from dilute solutions the bodies dissolved in them, this notion is exploded, and we now know that arable soil will retain with a certain force bodies otherwise soluble—from which we conclude that the aqueous extract of a soil cannot be expected to contain the whole of the substances present in that soil in a state immediately available for the plant. Neither can we expect to find these matters in the aqueous extract in the same proportion in which they are present in the soil, since the latter will readily give up to water those substances in regard to which its power of absorption has been satisfied, whilst it will more or less strongly retain others. But although, for this reason, the examination of the aqueous extract of a soil has no longer the same value as it was formerly considered to have, yet it is still useful to ascertain what substances a soil will actually give up to water. It is for this reason that I have retained the chapter on the preparation and examination of the aqueous extract.

‡ For more ample information on this subject the reader is referred to FRESENIUS's Chemie für Landwirthe, Forstmänner, und Cameralisten; Brunswick, Vieweg, 1847, p. 455.

1. *Preparation and Examination of the Aqueous Extract.*

§ 209.

About 1,000 grammes of the air-dried soil are used for 213
the preparation of the aqueous extract. To prepare this extract quite clear is a matter of some difficulty; in following the usual course, viz., digesting or boiling the earth with water, and filtering, the fine particles of clay are speedily found to impede the operation, by choking up the pores of the filter; they also almost invariably render the filtrate turbid, at least the portion which passes through first. I have found the following method proposed by F. SCHULZE (*loc. cit.*) the most practical: Close the neck of several middle-sized funnels with small filters of coarse blotting-paper, moisten the paper, press it close to the sides of the funnel, and then introduce the air-dried soil, in small lumps ranging from the size of a pea to that of a walnut, but not pulverized or even crushed, filling the funnels about two-thirds. Pour distilled water into them, in sufficient quantity to cover the soil; if the first portion of the filtrate is turbid, pour it back into the funnel. Let the operation proceed quietly. Fill the funnel again with water, and continue this process of lixiviation until the filtrates weigh twice or three times as much as the soil used. Collect the several filtrates in one vessel, and mix them intimately together. Keep a portion of the lixiviated soil.

Divide the aqueous solution into two parts, 1 (about two-thirds) and 2 (about one-third).

1. Evaporate in a porcelain dish to a small bulk, and test as follows:

a. Filter off a portion, test the reaction of the 214
filtrate, set aside a part to test for organic matter (224), warm the rest and add HNO_3. Effervescence indicates an ALKALI-METAL CARBONATE. Then test for CHLORINE with $AgNO_3$.

b. Transfer the rest of the concentrated fluid from 215
1, together with the precipitate which it usually contains, to a small dish (preferably of platinum), evaporate to dryness, and heat the brownish residue cau-

tiously till the organic matter is destroyed. In the presence of NITRATES a slight deflagration will be perceptible. Treat the residue as follows:

α. Test a small portion with Na_2CO_3 in the oxidizing flame for MANGANESE.

β. Warm the rest with water, add HCl (effervescence indicates carbonic acid), evaporate to dryness to separate silicic acid, moisten with HCl, add water, warm, and filter.

aa. Wash the residue, which generally contains a little carbon, a little clay (if the aqueous extract was not clear), and also SILICIC ACID. To detect the latter, pierce the filter, wash the residue through, boil it with NaOH, filter, saturate with HCl, evaporate to dryness, and finally take up with water, when the silicic acid will remain behind.

bb. Test a part of the HCl solution for SULPHURIC ACID with $BaCl_2$. Evaporate a second part with HNO_3 and test for PHOSPHORIC ACID with molybdic solution. Test a third part for IRON with KCNS. To the rest add a few drops of Fe_2Cl_6 (to remove phosphoric acid), then NH_4OH till slightly alkaline, warm a little, filter, throw down the CALCIUM with $(NH_4)_2C_2O_4$ and proceed to the examination for MAGNESIUM, POTASSIUM, and SODIUM (§§ 189, 190). Finally examine a small quantity of the pure alkali chlorides in the spectroscope for LITHIUM.

Aluminium is not likely to be found in the aqueous extract (F. SCHULZE never found it). To test for it, boil the precipitate produced by ammonia with pure KOH in a platinum dish, filter, acidify the filtrate with HCl, add NH_4OH, and warm. 216

2. If you have found iron, acidify a portion with HCl, and test half with $K_6Fe_2(CN)_{12}$, the other half with KCNS, to see in what state the iron is present. Mix the rest of the aqueous extract with a little H_2SO_4, evaporate nearly to dryness on the water bath, and test the residue for AMMONIA by $Ca(OH)_2$. If the aqueous 217

extract is absolutely clear you may test it for ammonia directly by $HgCl_2$, etc. (§ 92).

2. *Preparation and Examination of the Acid Extract.*

§ 210.

Heat about 50 grammes of the soil from which the part soluble in water has been removed as far as practicable* with moderately strong H Cl (effervescence indicates CARBONIC ACID) for several hours on the water bath, filter, and make the following experiments with the filtrate, which is generally yellow from the presence of ferric chloride: 218

1. Test a small portion with K C N S for tetrad IRON, another with $K_4 Fe_2 (CN)_{12}$ for dyad IRON. 219

2. Test a small portion with $BaCl_2$ for SULPHURIC ACID. Evaporate another portion to dryness, heat the residue to a temperature scarcely exceeding 100°, warm with HNO_3, filter off the silicic acid, and test for PHOSPHORIC ACID with molybdic solution in the cold.

3. Mix a large portion with NH_4OH to neutralize the free acid, then with yellowish ammonium sulphide; let the mixture stand in a warm place, in a flask filled up to the neck, until the fluid looks yellow; then filter, and test the filtrate in the usual way for CALCIUM, MAGNESIUM, POTASSIUM, and SODIUM. 220

4. Dissolve the precipitate obtained in 3 in H Cl, evaporate to dryness, moisten with H Cl, add water, warm, filter, and examine the filtrate according to **94**, for IRON, MANGANESE, ALUMINIUM, and if necessary, also for calcium and magnesium, which may have been thrown down by the ammonium sulphide in combination with phosphoric acid. 221

5. The separated SILICIC ACID obtained in 4 is usually colored by organic matter. It must, therefore, be ignited to obtain it pure.

6. If it is a matter of interest to ascertain whether the H Cl extract contains ARSENIC, COPPER, etc., treat 222

* Complete lixiviation is generally impracticable.

the remainder of the solution with H_2S, as directed **206-208.**

7. For FLUORINE, ignite a fresh portion, and proceed according to **174.**

3. *Examination of the Inorganic Constituents insoluble in Water and Acids.*

§ 211.

Heating the lixiviated soil with H Cl (**218**) leaves the **223** greater portion undissolved. To subject this undissolved residue to chemical examination, wash, dry, and sift, to separate the stones from the clay and sand; moreover, separate the two latter from each other by elutriation. Subject the several portions to the process given for silicates (§ 198).

4. *Examination of the Organic Constituents of the Soil.**

§ 212.

The organic constituents of the soil, which exercise so great an influence upon its fertility, both by their physical and chemical action, are partly portions of plants in which the structure may still be recognized (fragments of straw, roots, seeds of weeds, etc.), partly products of vegetable decomposition, which are usually called by the general name of HUMUS, but differ in their constituent elements and properties, according to whether they result from the decay of the nitrogenous or non-nitrogenous parts of plants—whether alkalies or alkali earths have or have not had a share in their formation—whether they are in the incipient or in a more advanced stage of decomposition. To separate these several component parts of humus would be an exceedingly difficult task, which, moreover, would hardly repay the trouble. The following operations are amply sufficient to answer all the purposes of a qualitative analysis:

* Compare FRESENIUS's Chemie für Landwirthe, Forstmänner, und Cameralisten; Brunswick, Vieweg, 1847, §§ 289-295.

a. Examination of the Organic Substances soluble in Water.

Evaporate the reserved portion of **214** on the water- **224**
bath to perfect dryness, and treat the residue with water. The humic acid, which was present in the solution in combination with bases, remains undissolved, whilst CRENIC AND APOCRENIC ACIDS are dissolved; for the manner of detecting the latter acids, see **212.**

b. Treatment with Alkali Carbonate.

Dry a portion of the lixiviated soil, and sift to separate **225**
the fragments of straw, roots, etc., and the small stones, from the finer parts; digest the latter for several hours at 80–90° with solution of sodium carbonate, and filter. Mix the filtrate with H Cl to acid reaction. If brown flakes separate, these proceed from HUMIC ACID.

c. Treatment with Caustic Alkali.

Wash the soil boiled with solution of sodium carbon- **226**
ate (*b*) with water, boil several hours with pure Na O H, replacing the water as it evaporates, dilute, filter, and wash. Treat the brown fluid as in *b*. The humic acid which separates now is a new product resulting from the action of boiling soda upon HUMIN.

V. Detection of Inorganic Substances in Presence of Organic Substances.

§ 213.

It will be readily conceived that the presence of organic substances may so far impede an analysis that it cannot be proceeded with until the organic matter has been rendered insoluble or totally destroyed; thus, for instance, the presence of organic coloring matter may completely conceal a change of color or a precipitate; again the presence of slimy matter may render filtration impossible. Difficulties of this kind are of constant occurrence in the examination of medicines, in the analysis of articles of food or of the contents of a stomach for in-

organic poisons, and in the analysis of the inorganic constituents of vegetable or animal substances. In the following pages instructions will be given first for a general procedure, afterwards for several special cases.

1. *General Rules for the Detection of Inorganic Substances in Presence of Organic matters, which by their Color, Consistence or other Properties, impede the Application of the Reagents, or obscure the Reactions produced.*

§ 214.

We confine ourselves here, of course, to the description of the most generally applicable methods, leaving the modifications which circumstances may require in special cases to the discretion of the analyst.

1. THE SUBSTANCE DISSOLVES IN WATER, BUT THE SOLUTION IS DARK-COLORED OR OF SLIMY CONSISTENCE. 227

a. Heat a portion of the solution with H Cl on the water bath, and gradually add $K Cl O_3$ until the mixture is decolorized and perfectly fluid; heat until it exhales no longer the odor of Cl, then dilute with water, and filter. Examine the filtrate in the usual way, commencing at § 183. Compare also § 218. It is hardly necessary to observe that mercurous, stannous, and ferrous salts would be changed to mercuric, stannic, and ferric chlorides respectively by this treatment.

b. Boil another portion of the solution for some time with $H N O_3$, filter, and test the filtrate for SILVER and POTASSIUM. If $H N O_3$ succeeds in effecting the ready and complete destruction of the coloring and slimy matters, etc., this method is often preferable to all others.

c. ALUMINIUM and CHROMIUM might escape detection by this method, because $N H_4 O H$ and $(N H_4)_2 S$ fail to precipitate their hydroxides from fluids containing non-volatile organic substances. Should you have reason to suspect the presence of these metals, mix a third portion of the substance with $Na C O_3$ and $K Cl O_3$ and throw the mixture gradually into a

red-hot crucible. Let the mass cool, then treat it with water, and examine the solution for chromic acid and aluminium, the residue for aluminium (§ 103).

d. Test a separate portion for AMMONIA with slacked lime.

e. Subject another portion to dialysis and examine the dialysate for acids.

2. BOILING WATER FAILS TO DISSOLVE THE SUBSTANCE, OR EFFECTS ONLY PARTIAL SOLUTION; THE FLUID ADMITS OF FILTRATION. **228**

Filter, and treat the filtrate either as directed § 182, or, should it require decoloration, according to **227**. The residue may be of various kinds.

a. It is FATTY. Remove the fatty matter by means of ether, and should a residue be left, treat this as directed § 175.

b. It is RESINOUS. Use alcohol instead of ether, or apply both liquids successively.

c. IT IS OF A DIFFERENT NATURE, *e.g.*, woody fibre, etc.

α. Dry and ignite a portion in a porcelain or platinum vessel, avoiding too high a temperature, until total or partial incineration is effected; warm the residue with H Cl and a little H N O, dilute and examine the solution as directed **53**; if a residue has been left, treat this according to § 196.

β. Examine another portion for the heavy metals and acids, as directed **227**—since with the method given in *α*, arsenic, cadmium, zinc, etc., may volatilize, besides mercury.

γ. Test the remainder for ammonia, by triturating with slacked lime.

3. THE SUBSTANCE DOES NOT ADMIT OF FILTRATION OR ANY OTHER MEANS OF SEPARATING THE DISSOLVED FROM THE UNDISSOLVED PART. **229**

Treat the substance in the same manner as the residue in **228**.

As regards the charred mass, **228** *c*, *α*, it is often advisable to boil the mass, carbonized at a gentle heat,

with water, filter, examine the filtrate, wash the residue, incinerate it, and examine the ash.

4. The following method proposed by E. MILLON * is of very general application for the detection of metals when mixed with organic matter. Transfer the substance to a tubulated retort and add four times its weight of pure H_2SO_4. The retort should not be more than one-third full. Heat slowly till the mixture is homogeneous, and then placing a funnel tube in the tubulure of the retort and gently increasing the temperature, add HNO_3 gradually. The object of this first operation is to decompose chlorides, which will take about half an hour. Now remove the mixture to a platinum dish and heat till the H_2SO_4, which by degrees loses its black color and turns orange or red, begins to escape. Add more HNO_3 in small portions; after each addition the fluid will be decolorized, but it again turns darker on further heating. Continue adding HNO_3 until no more coloration occurs, and finally expel the H_2SO_4, when you will obtain a saline mass to be analyzed in the usual way. If the heat is moderated towards the end, according to MILLON, none of the arsenic or mercury will be lost; but this cannot be depended on when much chlorides are present.†

5. To separate salts from colloid organic matter, dialysis is very convenient.‡ The substance is sometimes first warmed with HNO_3 or with $KClO_3$ and HCl. (Compare § 217.)

2. *Detection of Inorganic Poisons in Articles of Food, in Dead Bodies, etc., in Chemico-legal Cases.* §

§ 215.

The chemist is sometimes called upon to examine an 230
article of food, the contents of a stomach, a dead body, etc., with a view to detect the presence of some poison,

* Journ. de Pharm. et de Chim., 46, 33. Zeitschr. f. anal. Chem., 4, 208.

† GAUTIER'S process has, in many cases, great advantages. It is described in Fresenius' Quantitative Analysis., 2d Am. Edition, p. 783.

‡ Compare O. REVEIL. Zeitschr. f. anal. Chem.. 4, 266; BIZIO, *Ibid.* 5, 51; RIEDERER, *Ibid.*, 7, 517.

§ Compare FRESENIUS, Ann. d. Chem. u. Pharm., 49, 275; and FRESENIUS and v. BABO, Ann. d. Chem. u. Pharm., 49, 287.

and thus to establish the fact of poisoning; but it is more frequently the case that the question put to him is of a less general nature, and that he is called upon to determine whether a certain substance placed before him contains a metallic poison; or, more pointedly still, whether it contains arsenic or hydrocyanic acid, or some other particular poison—as it may be that the symptoms point clearly in the direction of that poison, or that the examining magistrate has, or believes he has, some other reason to put this question.

It is obvious that the task of the chemist will be the easier, the more special and pointed the question which is put to him. However, the analyst will always act most wisely, even in cases where he is simply requested to state whether a certain poison, *e.g.*, arsenic, is present or not, if he adopts a course of proceeding which will not only permit the detection of the one poison specially named, the presence of which may perhaps be suspected on insufficient grounds, but will moreover inform himself as to the presence or absence of other similar poisons.

But we must not go too far in this direction either; if we were to attempt to devise a method that should embrace all poisons, we might succeed in elaborating such a method at the writing-desk; but experience would speedily convince us that the complexity inseparable from such a course must impede the execution of the process and impair the certainty of the results, to such an extent that the drawbacks would be greater than the advantages derivable from it.

Moreover, the attendant circumstances permit usually at least a tolerably safe inference as to the group to which the poison belongs. Acting on these views, I give here—

1. A method which insures the detection of the minutest traces of arsenic, allows of its quantitative determination, and permits at the same time the detection of all other metallic poisons.

2. A method to effect the detection of hydrocyanic acid, which leaves the substance still fit to be examined both for metallic poisons and for alkaloids.

3. A method to effect the detection of phosphorus,

which does not interfere with the examination for other poisons.

This part of the work does not, therefore, profess to supply a complete guide in every possible case of chemico-legal investigations. But the instructions given in it are the tried and proved results of my own practice. Moreover, they will generally be found sufficient, the more so as in the Section on the alkaloids, I give the description of the best processes by which the detection of these latter poisons in criminal cases may be effected.

Where you have no indications at all of the sort of poison to be looked for, begin by carefully inspecting the substance, with the aid of a microscope if necessary, by noting the odor, reaction, etc., and then if the circumstances do not point to examining different portions for the different classes of poisons, proceed to test for hydrocyanic acid and phosphorus (a distillation usually suffices for the detection of both), afterwards for alkaloids, and finally for metallic poisons. As an obvious matter of caution, you should always reserve one-third of the substance, after weighing and mixing, for contingencies.

I. Method for the Detection of Arsenic (with due Regard to the possible Presence of other Metallic Poisons).

§ 216.

Of all metallic poisons arsenic is the most dangerous 231
and most frequently used for the wilful poisoning of others. Among the compounds of arsenic, arsenious oxide occupies the first place, because it kills even in small doses, it does not betray itself, or at least very slightly, by the taste, and it is readily procurable.

As arsenious oxide dissolves in water only sparingly, and—on account of the difficulty with which moisture adheres to it—very slowly, the greater portion of the quantity swallowed exists usually in the body in the undissolved state; as, moreover, the smallest grains of it may be readily detected by means of an exceedingly simple experiment; and lastly, as—no matter what opinion may be entertained about the normal presence of

arsenic in the bones, etc.—this much is certain, that *arsenious oxide in grains or powder* is never normally present in the body, the particular care and efforts of the analyst ought always to be directed to the detection of the arsenious oxide in substance—and this end may indeed usually be attained.

A. Method for the Detection of undissolved Arsenious Oxide.

1. If you have to examine food, vomit, or some other **232** matter of the kind, after weighing it mix the whole as uniformly as may be practicable, reserve one-third for contingencies, and mix the other two-thirds in a porcelain dish with distilled water, with a stirring rod; let the mixture stand a little, then pour off the fluid, together with the lighter suspended particles, into another porcelain dish. Repeat this latter operation several times, if possible with the same fluid, pouring it from the second dish back into the first and so on. Finally, wash once more with pure water, best in a glass dish, remove the fluid as far as practicable, and try whether you can find in the dish small, white, hard grains which feel gritty under the glass rod. If not proceed as directed § 217 or § 218. But if so, pick out the grains, or some of them, with a pair of pincers, or wash them if they are very minute in a watch glass, dry, weigh them, and heat a small portion in a glass tube, another small portion with a splinter of charcoal (compare § 132, 2 and 11). If you obtain in the former experiment a white sparkling sublimate consisting of octahedrons and tetrahedrons, in the latter experiment an arsenical mirror, you are quite safe in concluding that the grains consist of arsenious oxide. If you wish to determine the quantity of the arsenic, or to test for other metallic poisons, unite the contents of both dishes, and proceed as directed § 217 or § 218.

2. If a stomach is submitted to you for analysis, empty the contents into a porcelain dish, turn the stomach inside out, and (*a*), search the inside coat for small, white, hard sandy grains. The spots occupied by such grains are often reddened; the grains are also frequently found firmly imbedded in the membrane. (*b*) Mix the contents

in the dish uniformly, weigh them, put aside one-third for contingencies, and treat the other two-thirds as in 1. The same course is pursued also with the intestines. In other parts of the body—with the exception perhaps of the pharynx and œsophagus—arsenious oxide cannot be found in grains, if the poison has been introduced through the mouth. If you have found grains of the kind described, examine them as directed in 1; if not, or if you wish to test also for other metallic poisons, proceed according to § 217 or § 218.

B. Method of detecting soluble Arsenical and other Metallic Compounds by means of Dialysis.

§ 217.

If method *A* has failed to show the presence of arseni- 233
ous oxide in the solid state, and the process described in § 218, in which organic matter is coagulated or destroyed by potassium chlorate and hydrochloric acid, is at once resorted to, the operator must, of course, in the event of the presence of arsenic being revealed, give up all notion of ascertaining, as far as the portion operated upon is concerned, in what form the poison has been administered; as the process will give a solution containing arsenic acid, no matter whether the poison was originally present in that form, or as arsenious oxide, or as sulphide, or in the metallic state, etc. This defect may be remedied, however, by interpolating a dialytic experiment between *A* and *C*.

The experiment requires the apparatus shown in § 8, Fig. 5. The hoop is made of wood, or, better, of gutta-percha; it is 2 inches in depth, and 8 or 10 inches in diameter. The residue and fluid of § 216, *A*, having been mixed according to the circumstances with two-thirds of the stomach, intestinal canal, etc. (cut small and digested for twenty-four hours at about 32°), is poured into the dialyser to the depth of not more than half an inch. The dialyser is then floated in a basin containing about 4 times as much water as the fluid to be dialysed amounts to. After 24 hours one-half or three-fourths of the crystalloids will be found in the external water, which generally appears colorless. Concentrate this by evapora-

tion on the water bath, acidify the greater part with hydrochloric acid, treat with sulphuretted hydrogen, and proceed generally as directed **235** *et seq.* If an arsenical compound soluble in water (or some other soluble metallic salt) is present, the corresponding sulphide is obtained almost pure. By floating the dialyser successively on fresh supplies of water, the whole of the soluble crystalloids present may finally be withdrawn. If arsenic is found, test the remainder of the concentrated dialysate according to § 134, 9, to see whether arsenious or arsenic acid is present.

It is generally best to examine the exhausted contents of the dialyser at once according to § 218 for metals, but in some cases, as, for instance, when you wish to determine the state of oxidation or combination of compounds of arsenic or other metals, it is preferable to heat the matter first with dilute hydrochloric acid and to dialyse it again.

Instead of interpolating the dialysis at this stage, you may wait till the close of *C*, and then if a metallic poison has been found, and you wish to ascertain its state of combination, you may recur to this paragraph, using the reserved one-third for the experiment.

*C. Method for the Detection of Arsenic in whatever Form it may exist, which allows also of its Quantitative Determination, and of the Detection of all other Metallic Poisons.**

§ 218.

If you have found no arsenious oxide in substance by the method described in *A*, nor a soluble arsenical compound by dialysis, evaporate the mass in the porcelain dish, on the water bath, to a pasty consistence; adding,

* [The author's method is here given unchanged from the last edition. *So far as the detection and quantitative determination of arsenic are concerned*, this method is excessively tedious and complicated, and therefore unsatisfactory. No less than 12 reagents are employed when minute quantities of arsenic are to be looked for. Some of these are used in large quantities, and are often extremely difficult to obtain absolutely free from arsenic. This is especially true of H_2S and HCl.

GAUTIER'S process, as modified by JOHNSON and CHITTENDEN, on the other hand, is speedy and simple, requiring as reagents, besides water, only sulphuric and nitric acids, zinc and platinum, all of which may be purchased absolutely free from arsenic. This process is described in Fresenius' Quant. Anal., 2d Am. Ed., pp. 781-786, and more fully in Am. Chem. Journal, ii., 235, and v., 8.—ED.]

if occasion requires, two-thirds of the stomach and intestines cut small, provided this has not been done already in the process of dialysis.

In examining other parts of the body (the lungs, liver, etc.), cut them also into small pieces, and use two-thirds for the analysis.

The process is divided into nine parts.*

1. *Decoloration and Solution.*

234 Add to the matter in the porcelain dish, which may amount to, say 100 or 250 grammes, an amount of hydrochloric acid of 1.12 sp. gr., about equal to or somewhat exceeding the weight of the dry substances present, and sufficient water to give to the entire mass the consistence of a thin paste. The quantity of hydrochloric acid added should never exceed one-third of the entire liquid present. Heat the dish now on the water bath, adding every five minutes about two grammes of pure potassium chlorate to the hot fluid, with stirring, until the contents of the dish are light yellow, and also perfectly homogeneous and fluid; replace the evaporating water from time to time. When this point is attained, add again a portion of potassium chlorate, and then remove the dish from the water bath. When the contents are quite cold, transfer them cautiously to a linen strainer or a white filter, according to the quantity; allow the whole of the fluid to pass through, and heat the filtrate on the water bath with renewal of the evaporating water, until the smell of chlorine has gone off or nearly so. Wash the residue well with hot water, and dry it; then mark it I., and reserve for further examination, according to **247**. Evaporate the washings on the water bath to about 100 grammes, add this, together with any precipitate that may have formed therein, to the principal filtrate.

2. *Treatment of the Solution with Hydrosulphuric Acid.* (Separation of the Arsenic as Trisulphide, and of all the metals of Groups V. and VI. in form of Sulphides.) 235

Transfer the fluid obtained in 1, which amounts to three or four times the quantity of the hydrochloric acid

* I need hardly observe that, in an analysis of this kind, too much care cannot be taken to insure the purity of the reagents and the cleanliness of the apparatus.

used, to a flask, heat this on the water bath to 70°, and transmit through it, for about 12 hours, a slow stream of washed hydrosulphuric acid, then let the mixture cool, continuing the transmission of the gas; rinse the delivery pipe with some ammonia, add the ammoniated solution thus obtained, after acidifying, to the principal fluid, cover the flask lightly with unsized paper, and put it in a moderately warm place (about 30°) until the odor of hydrosulphuric acid has nearly disappeared. Collect the precipitate obtained in this manner on a filter, and wash with water containing hydrosulphuric acid until the washings are quite free from chlorine. Concentrate the filtrate and washings. If a precipitate forms, filter it off, wash and add to it the principal hydrosulphuric acid precipitate. Mix the concentrated fluid in a proper sized flask with ammonia to alkaline reaction, then with ammonium sulphide; closely cork the flask, which must now be nearly full, and reserve it for further examination according to **251.**

3. *Purification of the Precipitate produced by Hydrosulphuric Acid.*

236 The precipitate obtained in 2 contains the whole of the arsenic and all the other metals of the fifth and sixth groups, in the form of sulphides, and also organic matter and free sulphur. Dry it with the filter completely in a small dish, over the water bath, add pure fuming nitric acid (free from chlorine), drop by drop, until the mass is completely moistened, then evaporate on the water bath to dryness. Moisten the residue uniformly all over with pure concentrated sulphuric acid, previously warmed; then heat for two or three hours on the water bath, and finally with an air, sand, or oil bath at a somewhat higher, though still moderate temperature (170°), until the charred mass becomes friable, and a small sample of it—to be returned afterwards to the mass—when mixed with water and then allowed to subside, gives a colorless fluid; should the aqueous fluid be brownish, or should the residue consist of a brown oily liquid, add to the mass some cuttings of pure Swedish filtering paper, and continue the application of heat. You may raise the

heat till fumes of sulphuric acid begin to escape without fear of loss of arsenic. By attending to these rules you will always completely attain the object in view, viz., the destruction of the organic substances, without loss of any of the metals. Warm the residue on the water bath with a mixture of 8 parts of water and 1 part of hydrochloric acid, filter, wash the undissolved part thoroughly with hot water containing a little hydrochloric acid, and add the washings, concentrated if necessary, to the filtrate.

Dry the washed carbonaceous residue, then mark it II., and reserve it for further examination according to **248.**

4. *Preliminary Examination for Arsenic and other Metallic Poisons of Groups V. and VI.* (Second precipitation with Hydrosulphuric Acid.) **237**

The clear and colorless or, at the most, somewhat yellowish fluid obtained in 3, contains all the arsenic in form of arsenious acid, and may contain also tin, antimony, mercury, copper, bismuth, and cadmium. Supersaturate a small portion gradually with a mixture of ammonium carbonate and ammonia, and observe whether a precipitate is produced; acidify with hydrochloric acid, which will redissolve the precipitate that may have been produced by ammonia; then return the sample to the principal fluid, and treat the latter with hydrosulphuric acid, first at a gentle heat, afterwards without heat, according to **235.**

This process may lead to three different results, which are to be carefully distinguished.

a. The hydrosulphuric acid fails to produce a precipitate; but on standing a trifling white or yellowish-white precipitate separates. In this case probably no metals of Groups V. and VI. are present. Nevertheless, treat the filtered and washed precipitate as directed **241,** to guard against overlooking even the minutest traces of arsenic, etc. **238**

b. A precipitate is formed of a pure yellow color, like that of arsenious sulphide. Take a small portion of the fluid, together with the precipitate sus- **239**

pended therein, add some ammonia, and shake for some time without heating. If the precipitate dissolves readily and, with the exception of a trace of sulphur, completely, and if in the preliminary examination (**237**), ammonium carbonate has failed to produce a precipitate, arsenic alone is present, and no other metal (at least, if any tin or antimony is present, it is not worth mentioning). Mix the solution of the small sample in ammonia, with hydrochloric acid to acid reaction, return this to the fluid containing the principal precipitate and proceed as directed **241**. If, on the other hand, the addition of ammonia to the sample completely or partially fails to redissolve the precipitate, or if, in the preliminary examination (**237**), ammonium carbonate has produced a precipitate, there is reason to suppose that another metal is present, perhaps with arsenic. In this latter case, also, add to the sample in the test tube hydrochloric acid to acid reaction, return it to the fluid containing the principal precipitate, and proceed as directed **242**.

c. A precipitate is formed of another color. In that case you have to assume that other metals are present, perhaps with arsenic. Proceed as directed **242**. **240**

5. *Treatment of the yellow Precipitate produced by Hydrosulphuric Acid, when the Results of* **239** *lead to the Assumption that Arsenic alone is present.* (Determination of the Weight of the Arsenic.) **241**

As soon as the fluid precipitated according to **237** has nearly lost the smell of sulphuretted hydrogen, collect the yellow precipitate on a small filter, wash thoroughly, pour upon the still moist precipitate solution of ammonia, and wash the filter—on which, in this case, nothing must remain undissolved, except some sulphur—thoroughly with dilute ammonia; evaporate the fluid in a small accurately tared porcelain dish, on the water bath, and dry the residue at 100° until the weight is constant. The final weight represents the quantity of arsenious sulphide, if upon the subsequent reduction this

is found to be pure; in that case, multiply the weight by .8049 to obtain the corresponding amount of arsenious oxide, or by .6038 to obtain the corresponding amount of metallic arsenic. Treat the residue in the dish according to **244**.

6. *Treatment of the Yellow Precipitate produced by Hydrosulphuric Acid when the Results of* **239** *or* **240** *lead to the Assumption that another Metal is present—perhaps with Arsenic.* (Separation of the Metals from each other. Determination of the Weight of the Arsenic.) **242**

If you have reason to suppose that the fluid precipitated according to **237** contains other metals, perhaps with arsenic, proceed as follows: As soon as the precipitation is thoroughly accomplished, and the smell of sulphuretted hydrogen has nearly gone off, collect the precipitate on a small filter, wash thoroughly, pierce the filter, and wash all the precipitate into a small flask, using the least possible quantity of water; add to the fluid in which the precipitate is now suspended, first ammonia, then some yellowish ammonium sulphide, and let the mixture digest for some time at a gentle heat. Should part of the precipitate remain undissolved, filter this off, wash, pierce the filter, rinse off the residuary precipitate, mark it III., and reserve for further examination according to **249**. Evaporate the filtrate, together with the washings, in a small porcelain dish to dryness. Treat the residue with some pure fuming nitric acid (free from chlorine), nearly drive off the acid by evaporation, then add, as C. MEYER was the first to recommend, a solution of pure sodium carbonate, in small portions till in excess. Add now a mixture of 1 part of carbonate and 2 parts of nitrate of sodium in sufficient, yet not excessive quantity, evaporate to dryness, and heat the residue very gradually to fusion. Let the fused mass cool, and take it up with cold water. If a residue remains undis- **243**
solved, filter, wash with a mixture of equal parts of alcohol and water, mark it IV., and reserve for further examination, according to **250**. Mix the solution, which contains all the arsenic as sodium arsenate, with the washings, previously freed from alcohol by evaporation,

add cautiously pure dilute sulphuric acid to strongly acid reaction, evaporate in a small porcelain dish, and when the fluid is strongly concentrated, add again sulphuric acid, to see whether the quantity first added has been sufficient to expel all nitric acid and nitrous acid; heat now cautiously until heavy fumes of sulphuric acid begin to escape; then let the liquid cool, add water, transfer the solution to a small flask, keep heated at 70°, and conduct into it for at least 6 hours a slow stream of washed hydrosulphuric acid. Let the mixture finally cool, continuing the transmission of the gas all the while. If arsenic is present, a yellow precipitate will form. When the precipitate has completely subsided, and the fluid has nearly lost the smell of sulphuretted hydrogen, filter, wash the precipitate, dry it, extract the free sulphur with pure carbon disulphide, dissolve in ammonia, and treat the solution according to **241**, in order to determine the weight of the arsenic.

7. *Reduction of the Arsenious Sulphide.*

244 The production of metallic arsenic from the sulphide, which may be regarded as the keystone of the whole process, demands the greatest care and attention. The method recommended § 132, 12, viz., to fuse the arsenical compound, mixed with potassium cyanide and sodium carbonate, in a slow stream of carbon dioxide, is the best and safest, affording, besides the advantage of great accuracy, also a positive guarantee against the chance of confounding the arsenic with any other body, more particularly antimony; on which account it is especially adapted for medico-legal investigations.

Take care to have the whole apparatus filled with carbon dioxide, and to give the proper degree of force to the gaseous stream, before applying heat. The apparatus shown in Fig. 43, which has been described on p. 63, may be used. It is charged with lumps of marble, and with dilute H Cl. The current of gas is dried by passing through concentrated sulphuric acid in the small flask.

Do not reduce the whole of the arsenious sulphide at once, so that if you wish afterwards you may repeat the reduction several times. If there is too little arsenious

sulphide to be divided, dissolve it in a few drops of ammonia, add a small quantity of sodium carbonate, evap-

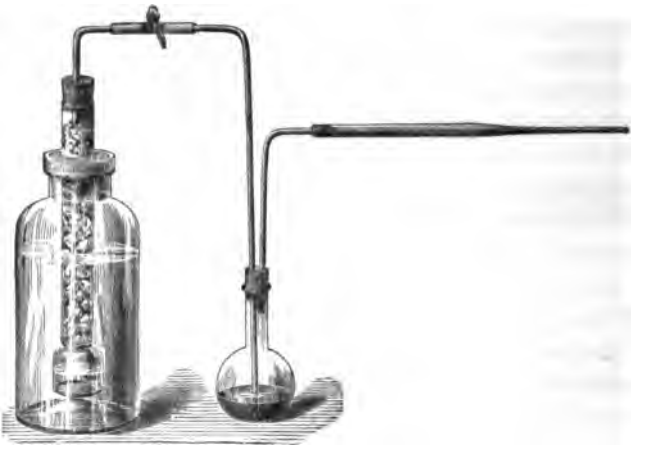


FIG. 43.

orate to dryness on the water bath with stirring, and take a portion of the mass for the reduction.

OTTO recommends* to convert the sulphide into an 245
arsenate, before proceeding to the reduction. The following is the process given by him to effect the conversion: Pour concentrated nitric acid over the sulphide in the dish, evaporate, and repeat the same operation several times if necessary, then remove every trace of nitric acid by repeatedly moistening the residue with water, and drying again, treat the residue with a few drops of water, add sodium carbonate in powder, to form an alkaline mass, and thoroughly dry this in the dish, with frequent stirring, taking care to collect the mass within the least possible space in the middle of the dish. The dry mass thus obtained is admirably adapted for reduction. I can fully confirm the statement; but I must once more repeat that it is indispensable for the success of the operation that the residue should be perfectly free from *every trace* of nitric acid or nitrate, since otherwise deflagration is sure to take place during the fusion with potassium cyanide, and, of course, the experiment will fail.

When the operation is finished, cut off the reduction 246

* Anleitung zur Ausmittelung der Gifte, von DR. FR. JUL. OTTO.

tube at *c* (Fig. 44), set aside the fore part, which contains the arsenical mirror, put the other part of the tube into a cylinder, pour water over it, and let it stand some time; then filter the solution obtained, add to the filtrate hydrochloric acid to acid reaction; then conduct some hydrosulphuric acid into it, and observe whether this produces a precipitate. In cases where the reduction of

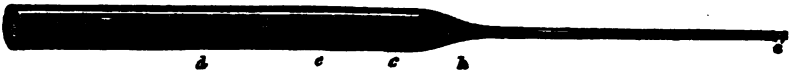


FIG. 44.

the arsenious sulphide has been effected directly, without previous conversion to arsenic acid, a trifling yellow precipitate will usually form; had traces of antimony been present, the precipitate would be orange-colored and insoluble in ammonium carbonate. After all the soluble salts of the fused mass have been dissolved out, examine the metallic residue which may be left, for traces of tin and antimony (nothing but traces of these two metals could be present here if the instructions given have been strictly followed). Should appreciable traces of these metals, or either of them, be found, proper allowance must be made for this in calculating the weight of the arsenic.

8. *Examination of the reserved Residues, for other Metals of the Fifth and Sixth Groups.*

Residue I. This may contain silver chloride and lead **247** sulphate, possibly also stannic oxide and barium sulphate. Incinerate it in a porcelain dish, burn the carbon with the aid of ammonium nitrate, extract the residue with water, dry the part left undissolved, then fuse it with sodium carbonate and potassium cyanide in a porcelain crucible. When cold exhaust with water, treat the residue with dilute acetic acid to extract any barium carbonate, warm any residue which may still be left with nitric acid, and proceed according to § 181. Test the acetic acid solution for barium with solution of calcium sulphate.

Residue II. This may contain lead, mercury, and tin, **248** possibly also antimony and bismuth. Heat it for some time with nitro-hydrochloric acid, and filter the solution; wash the residue with water, at first mixed with some hydrochloric acid, add the washings to the filtrate, and treat the mixture with hydrosulphuric acid. Should a precipitate form, examine it according to § 191. Incinerate the residue insoluble in nitro-hydrochloric acid, fuse the ash with potassium cyanide, and treat the fused mass as directed **247.**

Residue III. Examine for the metals of the fifth group **249** according to § 186.

Residue IV. This may contain tin and antimony, per- **250** haps also copper. Treat it as directed **67.** If the color of the residue was black (oxide of copper), treat the reduced metals according to § 181.

9. *Examination of the reserved filtrate for Metals of the Third and Fourth Groups, especially for Zinc, Chromium, and Thallium.**

a. The filtrate from the hydrosulphuric acid pre- **251** cipitate has already been mixed with ammonium sulphide. The addition of this reagent is usually attended with the formation of a precipitate consisting of iron sulphide and calcium phosphate, but which may possibly also contain zinc sulphide, thallium sulphide and chromic hydroxide. Filter it off, wash with water containing ammonium sulphide, dissolve by warming with hydrochloric acid and a little nitric acid, evaporate the filtrate with sulphuric acid in a retort till quite thick, and test the distillate with potassium iodide and platinic chloride, and also in the spectroscope, for THALLIUM (§ 113, *b*), as a portion of this metal may have escaped with the hydrochloric acid. Treat the residue in the retort with water, filter, add sodium carbonate to alkaline reaction, and then excess of solution of potassium cyanide

* With reference to the poisonous action of thallium, compare LAMY, Journ. f. prakt. Chem., 91, 366. And for the electrolytic method of discovering thallium in chemico-legal cases, see MARMÉ, Zeitschr. f. anal. Chem., 6, 503.

(free from sulphide). Heat for some time, filter, reserve the residue on the filter (α), mix the filtrate with ammonium sulphide, and examine the precipitate for THALLIUM in the spectroscope. Evaporate the filtrate together with the residue α under a good draught with excess of sulphuric acid, till some of the latter begins to escape, dilute, filter, throw down with ammonia and ammonium sulphide, and test the precipitate for ZINC and CHROMIUM according to **100–103.**

b. The fluid filtered from the precipitate produced **252** by ammonium sulphide (**251**) may contain all the chromium, as ammonium sulphide fails to precipitate chromic hydroxide completely from solutions containing organic matter. To detect it, evaporate to dryness, ignite, mix the fixed residue with 3 parts of potassium chlorate and 1 part of sodium carbonate, and project the mixture into a crucible heated to moderate redness. Allow the mass to cool, and boil with water, when a yellow coloration of the fluid will indicate chromium. For confirmatory tests see § 138.

II. METHOD FOR THE DETECTION OF HYDROCYANIC ACID.

§ 219.

Under the term hydrocyanic acid we include potassium **253** cyanide, which acts in the same way, and being extensively used in the arts is much more readily procurable. As hydrocyanic acid may easily decompose in presence of the matter of food or the contents of the stomach, the analyst must proceed without unnecessary delay. However, the acid does not decompose with such extreme rapidity as might be imagined, and in fact it is some time before the whole of it is lost.*

Although hydrocyanic acid betrays its presence, even in minute quantities, by its odor, still this sign must never be looked upon as conclusive. On the contrary, to adduce

* Thus I succeeded in separating a notable quantity of hydrocyanic acid from the stomach of a man who had poisoned himself with that acid in very hot weather, and whose intestines were not handed to me till 36 hours after death. Again, a dog was poisoned with hydrocyanic acid, and the contents of the stomach, mixed with the blood, were left for 24 hours exposed to an intense summer heat, and then examined: the acid was still detected.

positive proof of the presence of the acid, it is always indispensable to separate it, and to convert it into certain known compounds.

The method of accomplishing this, which I am about to describe, is based upon distillation of the acidified mass and examination of the distillate for hydrocyanic acid. Now, as the non-poisonous salts, potassium ferro- and ferricyanide, give by distillation likewise a product containing hydrocyanic acid, it is indispensable—as OTTO observes—first to ascertain whether one of these salts may not be present. To this end, stir a small portion of the mass to be examined with water, filter, acidify the filtrate with hydrochloric acid, and test a portion of it with ferric chloride, another with ferrous sulphate. If no blue precipitate or coloration forms in either, soluble ferro- and ferricyanides are not present, and you may safely proceed as follows. If a reaction is obtained, proceed according to **258.**

Test, in the first place, the reaction of the mass under **254** examination; if necessary, after mixing and stirring it with water. If it is not already strongly acid, add solution of tartaric acid until the fluid strongly reddens litmus paper; introduce the mixture into a retort, and place the body of the retort, with the neck pointing outwards, in an iron or copper vessel, the bottom of which is covered with a cloth; fill the vessel with a solution of calcium chloride, and apply heat, so as to cause gentle ebullition of the contents of the retort. Conduct the vapors passing over, with the aid of a tight-fitting tube bent at a very obtuse angle, through a LIEBIG'S condenser,* and receive the distillate in a small weighed flask. When about 15 c.c. of distillate has passed over, remove the receiver, and replace it by a somewhat large flask, also previously tared. Weigh the contents of the first receiver now, and proceed as follows:

a. Mix one-fourth with potassa to strongly alkaline **255** reaction, add a small quantity of solution of ferrous sulphate, mixed with a little ferric chloride, digest a few minutes at a very gentle heat, and supersaturate finally with hydrochloric acid. A blue precipitate

* In testing for phosphorus at the same time, the condenser must be entirely of glass, and the operation must be conducted in a perfectly dark room. Compare **262.**

indicates hydrocyanic acid. If only a very small quantity is present, the fluid is at first merely colored greenish, but on standing it will deposit blue flakes.

b. Treat another fourth as directed § 155, 7, to con- **256** vert the hydrocyanic acid into ferric sulphocyanide. As the distillate might, however, contain acetic acid, do not neglect to add at the end of the process a little more hydrochloric acid, in order to destroy the influence of the ammonium acetate.

c. If the experiments *a* and *b* have demonstrated **257** the presence of hydrocyanic acid, and you wish now also to approximately determine its quantity, continue the distillation as long as the fluid passing over contains hydrocyanic acid; add one-half of the contents of the second receiver to the remaining half of the contents of the first, mix the fluid with silver nitrate, then with ammonia in excess, and finally with nitric acid to strongly acid reaction. Allow the precipitate which forms to subside, collect on a tared filter dried at 100°, wash the precipitate, dry it thoroughly at 100°, and weigh. Ignite the weighed precipitate in a small porcelain crucible, to destroy the silver cyanide, fuse the residue with sodium carbonate (to effect the decomposition of the silver chloride which it may contain), boil the mass with water, filter, acidify the filtrate with nitric acid, and precipitate with silver nitrate; determine the weight of the silver chloride which may precipitate, and deduct the amount found from the total weight of the chloride and cyanide of silver. The difference gives the quantity of the latter; by multiplying this by .2017, you find the corresponding amount of anhydrous hydrocyanic acid; and by multiplying this again by 2—as only one-half of the distillate has been used—you find the total quantity of hydrocyanic acid which was present in the examined mass. Instead of decomposing the fused silver precipitate by fusion with sodium carbonate, it may be reduced also by means of zinc, with addition of dilute sulphuric acid, and the chlorine determined in the filtrate.

Instead of pursuing this indirect method, you may

also determine the quantity of the hydrocyanic acid by the following direct method: Introduce half of the distillate into a retort, together with powdered borax; distil to a small residue, and determine the hydrocyanic acid in the distillate as silver cyanide. Hydrochloric acid can no longer be present in this distillate, as the borax retains it in the retort (WACKENRODER).

When ferro- or ferricyanides have been detected, J. 258
OTTO recommends to slightly acidify the mass, to add precipitated calcium carbonate in excess, and to distil it at 40° or 50° on a water bath. The hydroferro- and hydroferricyanic acids are retained by the calcium of the calcium carbonate, the hydrocyanic acid distils over. The distillation cannot be effected directly over the flame, as hydrocyanic acid would pass into the distillate even when ferrocyanides or ferricyanides alone were present.

III. METHOD FOR THE DETECTION OF PHOSPHORUS.

§ 220.

Since phosphorus paste has been employed to poison 259
mice, etc., and the poisonous action of lucifer matches has become more extensively known, phosphorus has not unfrequently been resorted to as an agent for committing murder. The chemist is therefore occasionally called upon to examine some article of food, or the contents of a stomach, for this substance. It is obvious that, in cases of the kind, his whole attention must be directed to the separation of the phosphorus in the *free state*, or to the production of such reactions as will enable him to infer the presence of *free phosphorus*; since the mere finding of phosphorus in form of phosphates would prove nothing, as phosphates invariably form constituents of animal and vegetable bodies.

A. *Detection of Unoxidized Phosphorus.*

1. Ascertain in the first place whether the presence of 260
phosphorus is indicated by its smell, or by its luminosity

in the dark. To this end take care to increase the contact of the phosphorus with the air, by rubbing, stirring or shaking.

2. Put a little of the substance into a flask, fasten to **261** the loosely inserted cork a strip of filtering paper moistened with neutral solution of silver nitrate, and heat to 30° or 40°. If the paper does not turn black, even after some time, no unoxidized phosphorus is present, and there is consequently no need to try 3 and 4, but the operator may at once pass on to **268**. If, on the other hand, the paper turns black, this is no positive proof of the presence of phosphorus, as hydrosulphuric acid, formic acid, putrefying matters, etc., will also cause blackening of the paper. Treat therefore the principal mass of the substance now by the methods 3 and 4. (To ascertain whether the blackening proceeds from the presence of hydrosulphuric acid, try the reaction with a strip of paper moistened with solution of lead or with trichloride of antimony.)—T. SCHERER.*

3. As the luminosity of phosphorus is always one of **262** the most striking proofs of the presence of that element in the unoxidized state, examine a large portion of the substance by the following excellent and approved method recommended by E. MITSCHERLICH: †

Mix the substance with water and some sulphuric acid, or—if you are testing for hydrocyanic acid at the same time—tartaric acid, and subject the mixture to distillation in a flask *A* (Fig. 45). This flask is connected with an evolution tube *b*, and the latter again with a glass condensing tube, *c*, *c*, *c*, which passes through the bottom of a cylinder, *B*, in which it is fastened by means of a cork, and opens into a glass vessel *C*. Cold water is made to run from *D* through a stopcock, into a funnel *i*, the lower end of which rests upon the bottom of *B*; the water flows off through *g*.‡

Now if the substance in *A* contains phosphorus, there will appear, in the dark, at the point *r*, a strong luminosity, usually a luminous ring. If you take for distilla-

* Ann. d. Chem. u. Pharm., 112, 214.

† Journ. f. prakt. Chem., 66, 238.

‡ A glass LIEBIG's condenser may of course be used instead of this apparatus.

tion 150 grm. of a mixture containing only 1.5 mgrm. of phosphorus, and accordingly only 1 part in 100,000, you

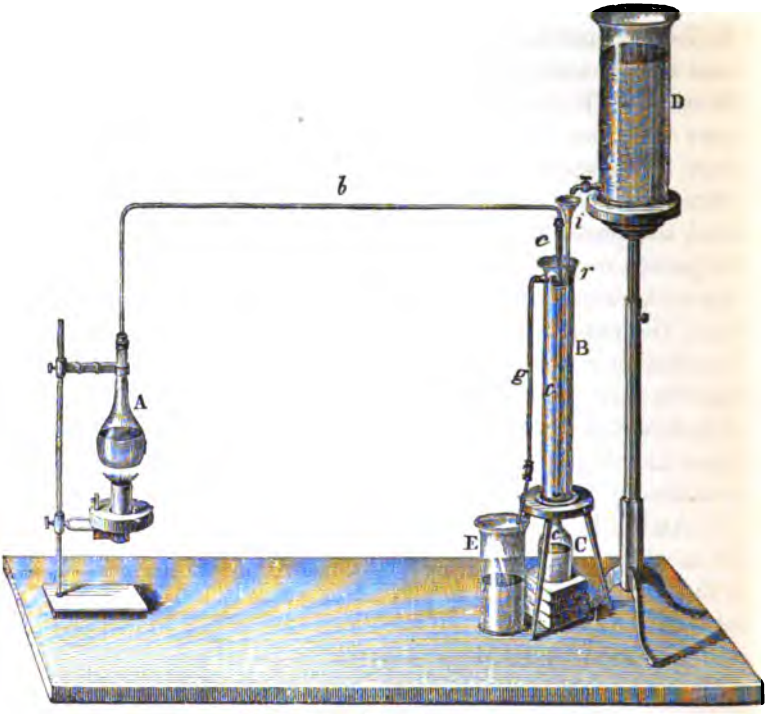


FIG. 45.

may distil over 90 grm., which will take at least half an hour, without the luminosity ceasing. MITSCHERLICH, in one of his experiments, stopped the distillation after half an hour, allowed the flask to stand uncorked for a fortnight, and then recommenced the distillation; the luminosity was as strong as at first.

If the fluid contains substances which prevent the luminosity of phosphorus, such as ether, alcohol, or oil of turpentine, no luminosity is observed so long as these substances continue to distil over. In the case of ether and alcohol, however, this is soon effected, and the luminosity accordingly very speedily makes its appearance; but oil of turpentine positively stops the reaction.

After the termination of the process, globules of phos- 263

phorus are found at the bottom of the receiver. MITSCHERLICH obtained from 150 grm. of a mixture containing .02 grm. phosphorus, so many gobules of that body, that the tenth part of them would have been amply sufficient to demonstrate its presence. In medico-legal investigations these globules should first be washed with alcohol, then weighed. A portion may afterwards be subjected to a confirmatory examination, to make quite sure that they really consist of phosphorus; the remainder, together with a portion of the fluid which shows the luminosity upon distillation, should be sent in with the report.

The operation should be conducted in a dark place, best in the evening. Where it is performed in the daytime, care should be taken to close all avenues to the entrance of light, as where this not effectively done, the rays of light, entering through some chink or crevice, may chance to be reflected by the glass vessel or by the fluids, and thus lead to deception. It is advisable to pass the evolution tube at *b*, through the aperture of a screen, to guard effectively against reflection of light from the lamp. These precautionary measures are of course necessary only where very minute traces of phosphorus are to be detected.

The residue left in the flask is then examined for phosphorous acid as directed **268.** The distillate also may be further examined in the same way, to confirm the presence of phosphorus, or to show the presence of phosphorous acid formed by the oxidation of phosphorus fumes.*

4. Put another portion of the substance, with addition **264** of water if necessary, into a flask with doubly perforated cork, add dilute sulphuric acid to acid reaction, conduct washed carbon dioxide (evolved most conveniently from the evolution apparatus shown p. 398) in a slow stream, into the flask, through a glass tube reaching nearly to the bottom, and let the gas issuing from another glass tube, inserted into the other perforation of the cork, pass through one or two U tubes containing a neutral solution of silver

* In testing for hydrocyanic acid at the same time, it is best to collect the first 15 c.c. of the distillate separately, and to examine this for hydrocyanic acid, the subsequent portions for phosphorus.

nitrate. When the flask is filled with carbon dioxide, heat it gently on the water bath. Continue the operation for several hours. If free phosphorus is present, it will volatilize unoxidized in the stream of carbon dioxide, then pass into the silver solution, where it will be partly converted into black silver phosphide, partly into phosphoric acid. If no precipitate forms, you may safely conclude that no unoxidized phosphorus is present, whilst, on the other hand, the formation of a precipitate is not sufficient proof of the presence of phosphorus, as the precipitate may owe its formation to volatile reducing agents or to hydrosulphuric acid.

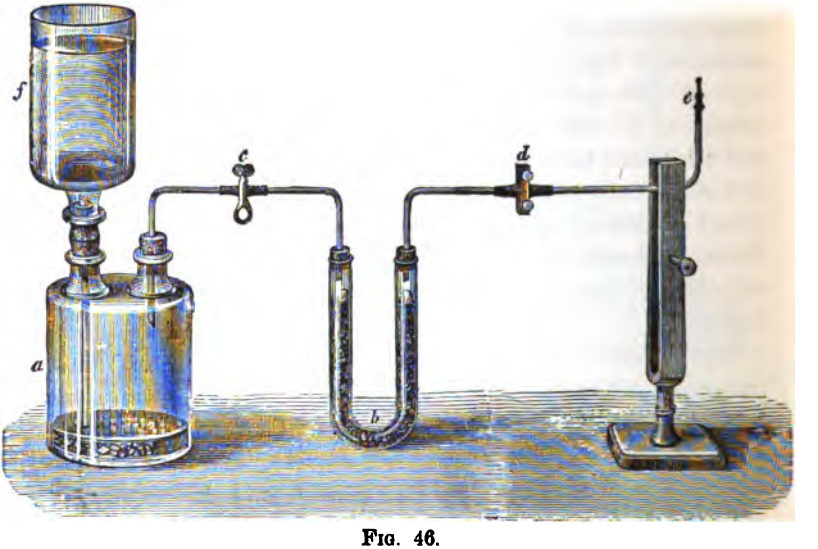


FIG. 46.

If a precipitate has formed, filter through a filter well 265
washed with dilute nitric acid and water, and wash. The presence of silver phosphide in it may be shown by BLONDLOT'S improved modification of DUSART'S method,* substituting, however, for the apparatus used by BLONDLOT, the one shown (Fig. 46), which may be easily constructed.

a is a hydrogen-evolution bottle, *b* contains pumice-stone moistened with concentrated solution of potassa, *c* is a common clip, *d* is a screw clip, *e* a platinum jet, which

* Zeitschr. f. anal. Chem., 1, 129.

is kept cool by tying moistened cotton round it. This plantinum jet is indispensable to the production of a colorless hydrogen flame, as the soda in the glass will always color the flame yellow.

To ascertain whether the zinc and sulphuric acid will give a gas quite free from phosphuretted hydrogen, let the evolution go on a short time, then close *c* until the fluid has ascended from *a* to *f*. Close *d*, open *c*, and regulate *d* by means of the screws so as to obtain a suitable flame. If the flame, viewed in a dark place, is colorless, showing no trace of a green cone in the centre, and no emerald-green coloration when pressed upon by a piece of porcelain, as in MARSH'S experiment, the hydrogen may be considered pure. It is advisable to repeat the experiment. Rinse the precipitate under examination into *f*, take care that every particle of it reaches *a*, then repeat the experiment again. If the precipitate contains even a minute trace of silver phosphide, the green cone in the centre of the flame and the emerald-green coloration will now become distinctly visible.

Remove the excess of silver from the solution filtered **266** from the silver precipitate, by hydrochloric acid, pass through a filter well washed with acid and water, remove the hydrochloric acid by evaporation on the water bath, take up with nitric acid, and test for phosphoric acid with molybdic solution, or with a mixture of magnesium sulphate, ammonium chloride, and ammonia (NEUBAUER and FRESENIUS).*

We obtained by this method the clearest evidence of the presence of phosphorus in a large quantity of putrid blood mixed with the head of a common lucifer match; and this even in presence of substances which prevent the luminosity of the phosphorus in MITSCHERLICH'S method.

5. If there is sufficient phosphorus present to permit **267** a quantitative determination, this may be effected by SCHERER'S modification of MITSCHERLICH'S method, viz., by distilling the mass, acidified with sulphuric acid, in an atmosphere of carbon dioxide. I would suggest, with respect to this, to have the distilling flask furnished with a doubly perforated cork, and to transmit pure carbon

* Zeitschr. f. anal. Chem., 1, 336.

dioxide until the apparatus is filled with it, but then to shut off the gas stream. A flask with doubly perforated cork serves for receiver; the mouth of the condensing tube passes into one of the openings; into the other is inserted a bent glass tube, which leads to a U tube containing a solution of pure silver nitrate.

When the distillation is over, minute globules of phosphorus are found in the receiver. A moderate stream of carbon dioxide is now once more transmitted through the apparatus, and a gentle heat applied, with a view to effect the formation of larger globules by aggregation. These are then washed and weighed as in MITSCHERLICH'S method. The fluid poured off the phosphorus globules is luminous in the dark when shaken. It requires, however, a larger proportion of phosphorus to obtain distinct luminosity in this way than is the case with MITSCHERLICH'S method. The phosphorus in the fluid may, after oxidation by nitric acid or chlorine, be determined as phosphoric acid. However, the result is reliable only if the operation has been conducted with the requisite care to guard against the spirting over of portions of the boiling fluid, which often contains phosphoric acid. To obtain the remainder of the phosphorus, treat the contents of the U tube with nitric acid, throw down the silver by hydrochloric acid, filter through a washed filter, concentrate in a porcelain dish, precipitate the phosphoric acid as ammonium magnesium phosphate, and weigh it as magnesium pyrophosphate.

B. *Detection of Phosphorous Acid.*

Should all attempts to detect phosphorus fail, try **268** whether it may not be practicable to find the first product of its oxidation, *i.e.*, phosphorous acid. For this purpose transfer the residue left in the distilling flask in **262** or in **267**, or the residue left in **264**, to the apparatus illustrated by Fig. 46, having previously tested the purity of the zinc and sulphuric acid, then proceed according to the instruction of **265**, and observe whether the coloration of the hydrogen flame reveals the presence of phosphorus (WÖHLER). Should this be the case, the end in view is attained; if not, the presence of organic sub-

stances may be the preventive cause. If, therefore, the flame remains uncolored, shut the clip at once, connect with the apparatus a U tube containing neutral solution of silver nitrate, open the clip again, and let the gas pass for many hours, in a slow stream, through the silver solution. If phosphorous acid is present, a precipitate containing silver phosphide will separate in the silver solution; examine it according to **265.***

3. *Examination of the Inorganic Constituents of Plants, Animals, or Parts of the same, of Manures, etc. (Analysis of Ashes).*

§ 221.

A. Preparation of the Ash.

269 It is sufficient for the purposes of a qualitative analysis to incinerate a comparatively small quantity of the substance, which must previously be most carefully cleaned. The incineration is effected best in a small clay muffle, but it may be conducted also in a Hessian crucible placed in a slanting position, or under certain circumstances, even in a porcelain or platinum dish, with the aid of a wide glass tube or lamp-glass, to increase the draught. The heat must always be moderate, to prevent the volatilization of certain constituents, especially of chlorides. It is not always necessary to continue the combustion until all the carbon is consumed. With ashes containing a large proportion of fusible salts, as the ash of beet-root molasses, it is best, after thorough carbonization has been effected, to boil with water, and finally to incinerate the washed and dried residue. For further particulars see *Quantitative Analysis.*

B. Examination of the Ash.

270 As the qualitative analysis of an ash is undertaken, either as a practical exercise, or for the purpose of

* W. Herapath's statement (Pharm. Journ., 1865, 573), that phosphoric acid is also reduced by zinc and dilute sulphuric acid, I have not found to be in accordance with the facts. Compare my paper in the Zeitschr. f. anal. Chem., 6, 203.

determining its general character, and the state in which any given constituent may happen to be present, or also with a view to make, as far as practicable, an approximate estimation of the quantities of the several constituents, it is usually the best way to examine separately the part soluble in water, the part soluble in hydrochloric acid, and the residue which is insoluble in both. This can be done the more readily, as the number of bodies to be looked for is but small.

a. Examination of the Part soluble in Water.

Boil the ash with water, filter, and whilst the residue is being washed, examine the solution as follows:

271 1. Add to a portion, after heating it, H Cl in excess, warm, and allow to stand. Effervescence indicates CARBONIC ACID combined with alkali metals; smell of H_2S indicates the SULPHIDE OF AN ALKALI METAL, formed from an alkali sulphate by the reducing action of carbon. Turbidity from separation of sulphur, with smell of sulphur dioxide, denotes a THIOSULPHATE (HYPOSULPHITE) (which occurs occasionally in the ash of coal). Filter if necessary, and add $BaCl_2$ to the fluid; a white precipitate indicates SULPHURIC ACID.

272 2. Evaporate another portion to a small volume, add H Cl to acid reaction (effervescence indicates CARBONIC ACID), test a few drops for BORIC ACID with turmeric, evaporate to dryness, and treat the residue with H Cl and water; a residue consists of SILICIC ACID. Filter, add NH_4OH and magnesium mixture; a white precipitate indicates PHOSPHORIC ACID. Instead of this reaction, you may also mix the fluid filtered from the silicic acid with sodium acetate, and then cautiously add ferric chloride, or you may evaporate with excess of HNO_3 on the water bath to dryness, treat the residue with HNO_3, and test with molybdic solution (§ 142).

273 3. Add to another portion $AgNO_3$ as long as a precipitate continues to form; warm gently, and then cautiously add NH_4OH; if a black residue is left, this consists of silver sulphide, proceeding from the sulphide of an alkali metal, or from a thiosulphate. Filter, if necessary,

add HNO_3 in slight excess, to effect the solution of the silver phosphate precipitate formed, leaving thus only SILVER CHLORIDE (iodide, * bromide) undissolved. Filter and examine the precipitate as directed **122**, neutralize the filtrate exactly with ammonia. If this produces a light-yellow precipitate, orthophosphoric acid was present; if a white precipitate, pyrophosphoric acid was present in **272**.

4. Heat a portion with HCl, then make it alkaline with **274** NH_4OH; mix with $(NH_4)_2C_2O_4$, and allow to stand. A white precipitate indicates CALCIUM. Filter and mix the filtrate with NH_4OH and Na_2HPO_4; a crystalline precipitate, which often becomes visible only after long standing, indicates MAGNESIUM. (Magnesium is often found in distinctly appreciable, calcium only in exceedingly minute quantity, even where alkali carbonates and phosphates are present.)

5. For POTASSIUM and SODIUM examine as directed § 190. If magnesium is present, first neutralize with hydrochloric acid, and remove the magnesium as directed § 189, 2.

6. LITHIUM, which is much more frequently found in ashes than has hitherto been believed, and RUBIDIUM, which almost constantly accompanies potassium, may be most readily detected by the spectroscope in the residue consisting of the alkali salts.

b. Examination of the Part soluble in Hydrochloric Acid.

Warm the residue left undissolved by water with HCl † **275** —effervescence indicates CARBONIC ACID accompanied with alkali-earth metals; evolution of Cl denotes OXIDES OF MANGANESE. Evaporate to dryness with a few drops of H_2SO_4, heat a little more strongly to separate the SILICIC ACID, moisten the residue with HCl and some HNO_3, add water, warm, and filter. Examine the precipitate for BARIUM and STRONTIUM according to **199**. Examine the solution as follows:

* To detect the iodine in aquatic plants, dip the plant in weak solution of potassa (CHATIN), dry, incinerate, treat with water, and examine the solution as directed (**258**).

† If the residue still contains much carbon, after further incineration.

1. Test a portion with H_2S. If this produces any other than a perfectly white precipitate, you must examine it in the usual way. (The ashes of plants occasionally contain COPPER; if the plant has been manured with excrements deodorized by lead nitrate, they may contain LEAD, and so on.)

2. Mix a portion with Na_2CO_3, as long as the precip- **276**
itate formed redissolves upon stirring; then add sodium acetate, and some acetic acid. This produces, in most cases, a white precipitate of FERRIC PHOSPHATE, mixed occasionally with ALUMINIUM PHOSPHATE. Filter, wash the precipitate, heat it with pure KOH, filter and test the filtrate for ALUMINIUM by acidifying with HCl, adding NH_4OH, and warming. If the filtrate is reddish, there is more iron present than corresponds to the phosphoric acid; if it is colorless, add ferric chloride drop by drop till the fluid is reddish. (The quantity of the precipitate of ferric phosphate here formed will give you some idea of the amount of PHOSPHORIC ACID present.) Boil, if the fluid does not lose its color, add more sodium acetate and boil again, filter hot, neutralize the filtrate exactly with NH_4OH, mix with $(NH_4)_2S$ in a flask, fill up the latter, close the mouth, allow to stand some time and filter. Test the precipitate according to **85** for MANGANESE and ZINC (the latter is seldom present); test the filtrate for CALCIUM and MAGNESIUM (**274**). The calcium may contain a little STRONTIUM, and must therefore be tested according to p. 131.

Test the rest for *fluorine* according to § 146, 6.

c. *Examination of the Residue insoluble in Hydrochloric Acid.*

The residue insoluble in HCl contains:

1. The silicic acid, which has separated on treating **277**
with HCl.

2. Those ingredients of the ash which are insoluble in HCl. These are, in most ashes, sand, clay, carbon; substances, therefore, which are present in consequence of defective cleaning or imperfect combustion of the plants, or matter derived from the crucible. It is only the ashes

of the stalks of cereals and others abounding in silicic acid that are not completely decomposed by H Cl.

Boil the washed residue with solution of Na_2CO_3 in excess, filter hot, wash with boiling water, and test for silicic acid in the filtrate by evaporation with H Cl (§ 150, 2). If the ash was of a kind to be completely decomposed by H Cl, the analysis may be considered finished—for the accidental admixture of clay and sand will rarely interest the analyst sufficiently to warrant a more minute examination by fusing. But if the ash abounded in silicic acid, and it may therefore be supposed that the H Cl has failed to effect complete decomposition, evaporate half of the residue insoluble in solution of Na_2CO_3 with pure solution of Na OH in excess, in a silver or platinum dish, to dryness. This decomposes the silicates of the ash, whilst but little affecting the sand. Acidify now with H Cl, evaporate to dryness, etc., and proceed as in **275**. For the detection of the alkalies use the other half of the residue, treating this according to **172**. **278**

SECTION III.

EXPLANATORY NOTES AND ADDITIONS TO THE SYSTEMATIC COURSE OF ANALYSIS.

I. Additional Remarks to the Preliminary Examination.

To §§ 175–178.

The inspection of the physical properties of a body may, as already stated, in many cases enable the analyst to draw certain general inferences as to its nature. Thus, for instance, if the analyst has a white substance before him, he may at once conclude that it is not cinnabar, or if a light substance, that it is not a compound of lead, etc. Inferences of this kind are quite admissible to a certain extent; but if carried too far, they are apt to mislead the operator, by blinding him to every reaction not exactly in accordance with his preconceived notions.

As regards the examination of substances at a high temperature, platinum foil or small iron spoons may also be used in the process; however, the glass tube gives, in most cases, results more clearly evident, and affords moreover the advantage that volatile bodies are less likely to escape detection. To ascertain the products of oxidation of a body it is sometimes advisable also to heat it in a short glass tube, open at both ends, and held in a slanting position; small quantities of a metallic sulphide, for instance, may be readily detected by this means (§ 156, 6).

With respect to the preliminary examination by means of the blowpipe, I have to remark that the student must avoid drawing positive conclusions, until he has acquired some practice. A slight incrustation of the charcoal, which may seem to denote the presence of a certain metal, is not always a conclusive proof of the presence of that metal; nor would it be safe to assume the absence of a substance simply because the blowpipe flame fails to effect reduction, or solution of cobalt nitrate fails to impart a color to the ignited mass, etc. The blowpipe reactions are, indeed, in most cases, unerring, but it is not always easy to produce them, and they are moreover liable to suffer modification by accidental circumstances.

The student should never omit the preliminary examination; the notion that this omission will save time and trouble is very erroneous.

II. Additional Remarks to the Solution, etc., of Substances.

To §§ 179–181.

It is a task of some difficulty to fix the exact limit between substances which are soluble in water and those that are insoluble in that menstruum, since the number of bodies which are sparingly soluble in water is very considerable, and the transition from sparingly soluble to insoluble is very gradual. Calcium sulphate, which is soluble in 430 parts of water, might perhaps serve as a limit between the two classes, since this salt may still be positively detected in aqueous solution by the delicate reagents which we possess for calcium and sulphuric acid.

When examining an aqueous fluid by evaporating a few

drops of it upon platinum foil, to see whether it holds a solid body in solution, a very minute residue sometimes remains, which leaves the analyst in doubt respecting the nature of the substance. In cases of the kind test, in the first place, the reaction of the fluid with litmus papers; in the second place, add to a portion of it a drop of solution of $Ba\,Cl_2$; and lastly, to another portion some $Na_2\,C\,O_3$. Should the fluid be neutral, and remain unaltered upon the addition of these reagents, the analyst need not, as a general rule, examine it any further for bases or acids; since if the fluid contained any of those bases or acids which principally form sparingly soluble compounds, $Ba\,Cl_2$ and $Na_2\,C\,O_3$ would have revealed their presence. The analyst may therefore feel assured that the detection of the substance of which the residue left upon evaporation consists will be more readily effected in the class of bodies insoluble in water.

If water has dissolved any part of the substance under examination, the student will always do well to examine the solution both for acids and bases, since this will lead more readily to a correct apprehension of the nature of the compound and will give greater certainty—two advantages which will amply counterbalance the drawback of sometimes meeting with the same substance both in the aqueous and in the acid solution.

The following substances (with few exceptions) are insoluble in water, but soluble in $H\,Cl$ or in $H\,N\,O_3$: the phosphates, arsenates, arsenites, borates, carbonates and oxalates of all but the alkali metals; also several tartrates, citrates, malates, benzoates and succinates; the oxides, hydroxides, and sulphides of the heavy metals; alumina, magnesia; many of the metallic iodides and cyanides, etc. Nearly the whole of these compounds are indeed, decomposed, if not by dilute, by boiling concentrated $H\,Cl$;* but this decomposition gives rise to the formation of insoluble compounds where silver is present, and of sparingly soluble compounds in the presence of mercury (as mercurous salts) and lead. This is not the case with $H\,N\,O_3$, and accordingly the latter effects complete solution in many cases where $H\,Cl$ leaves a residue. On the other hand, however, $H\,N\,O_3$ leaves, besides the bodies insoluble in any simple acid, antimonious oxide, metastannic

* For the exceptions, see § 196.

acid, lead dioxide, etc., undissolved, and dissolves many other substances less readily than H Cl—*e.g.*, ferric oxide and alumina.

Substances not soluble in water are therefore, briefly, to be treated as follows: Try to dissolve them in dilute or concentrated, cold or boiling H Cl; if this fails to effect complete solution, try to dissolve a fresh portion in HNO_3; if this also fails, treat the body with aqua regia, which is an excellent solvent, more particularly for metallic sulphides. To examine separately the solution in H Cl or in HNO_3, on the one hand, and that in nitro-hydrochloric acid on the other, is in most cases, neither necessary nor desirable. To prepare a solution in HNO_3 or in aqua regia, where the nature of the substance does not absolutely demand it, is not advisable, as a solution in H Cl is much better suited for precipitation by H_2S. Nor is it advisable to concentrate a solution in aqua regia by evaporation, to drive off the excess of the acids, as the operation might lead to the escape of volatile chlorides, more particularly of $AsCl_3$. It is therefore always best to use no more aqua regia than is just necessary to effect solution. Solutions prepared with H Cl generally contain the metals in the same state in which they were originally present (Hg_2Cl_2 by protracted boiling with H Cl, gradually decomposes into Hg and $HgCl_2$). On the other hand, solutions prepared with HNO_3 or aqua regia, frequently contain the metals in a higher state of quantivalence, thus, for instance, ferrous, stannous, and arsenious compounds are converted into ferric, stannic, and arsenic compounds.

With regard to the solution of metals and alloys, I have to remark that, upon boiling them with HNO_3, white precipitates will frequently form, although neither tin nor antimony be present. Inexperienced students often confound such precipitates with the hydroxides of these two metals, although their appearance is quite different. These precipitates consist simply of nitrates sparingly soluble in the HNO_3 present, but readily soluble in water. Consequently the analyst should ascertain whether these white precipitates will dissolve in water or not, before he concludes that they consist of tin or antimony.

III. Additional Remarks to the Actual Analysis.

To §§ 182–196.

A General Review and Explanation of the Analytical Course.

a. Detection of the Metals.

The classification of the metals into groups, and the methods which serve to detect and isolate them individually, have been fully explained in Part I., Section III. The systematic course of analysis, from § 182 to § 191, is founded upon this classification of the metals; and as a correct apprehension of it is of primary importance, I will here subjoin a brief explanation of the grounds upon which this division rests. Respecting the detection of the several metals individually, I refer the student to the recapitulations and separations in §§ 92, 99, *et seq.*

The general reagents which serve to divide the metals into principal groups are: HYDROCHLORIC ACID, HYDROSULPHURIC ACID, AMMONIUM SULPHIDE, and AMMONIUM CARBONATE; this is likewise the order of succession in which they are applied. Ammonium sulphide performs a double part.

Let us suppose we have in solution the whole of the metals, including both triad and pentad arsenic, and also calcium phosphate, which latter may serve as a type for the salts of the alkali-earth metals, soluble in acids and reprecipitated unaltered by $N H_4 O H$.

Chlorine forms insoluble compounds only with silver and mercury (in mercurous state); lead chloride is sparingly soluble in water. If, therefore, we add to our solution:

1. *Hydrochloric Acid,*

we remove from it the metals of the first division of the fifth group, viz., the whole of the SILVER and the whole of the MERCURY existing in MERCUROUS form. From concentrated solutions a portion of the LEAD may likewise precipitate as chloride; this is, however, immaterial, as a sufficient quantity of the lead remains in the solution to permit the subsequent detection of this metal.

Hydrosulphuric acid completely precipitates the metals of

the fifth and sixth groups from solutions containing a free mineral acid, EVEN THOUGH THE ACID BE PRESENT IN EXCESS. But none of the other metals are precipitated under these circumstances, since those of the first and second groups form no insoluble sulphur compounds; the sulphides of the third group (aluminium sulphide and chromium sulphide) cannot be formed in the humid way; while those of the fourth group cannot exist in presence of A STRONG ACID IN THE FREE STATE.

If, therefore, after the removal of silver and (mercurous) mercury, by means of hydrochloric acid, we add to the solution, which still contains free hydrochloric acid,

2. *Hydrosulphuric Acid,*

we remove from it the remainder of the metals of the fifth, together with those of the sixth group, viz., LEAD, (mercuric) MERCURY, COPPER, BISMUTH, CADMIUM, GOLD, PLATINUM, TIN, ANTIMONY, and ARSENIC. All other metals remain in solution.

The sulphides (at least the higher sulphides) of the metals of the sixth group combine with the sulphides of the alkali metals, and form sulphur salts soluble in water; while the sulphides of the metals of the fifth group do not possess this property, or possess it only to a limited extent.* If, therefore, we treat the whole of the sulphides precipitated by hydrosulphuric acid from an acid solution, with—

3. *Ammonium Sulphide,*

with addition, if necessary, of some sulphur or yellow ammonium sulphide, the sulphides of mercury, lead, bismuth, and cadmium remain entirely, and that of copper partially undissolved, whilst the other sulphides dissolve completely as compounds of sulphide of GOLD, PLATINUM, ANTIMONY, TIN, ARSENIC, with ammonium sulphide, and precipitate again from this solution upon the addition of hydrochloric acid, either unaltered or in a state of higher sulphuration (they take up sulphur from the yellow ammonium sulphide). The rationale of this precipitation is as follows: The acid decomposes the sulphur salt formed. The sulphur base (ammonium sul-

* Mercuric sulphide combines with potassium sulphide and sodium sulphide, but not with ammonium sulphide. Cupric sulphide is more or less reduced to cuprous sulphide by ammonium sulphide and unites to it, but is unaffected by potassium sulphide or sodium sulphide.

phide) is decomposed by hydrochloric acid into (ammonium) chloride and hydrosulphuric acid; and the liberated sulphur acid precipitates. Sulphur precipitates at the same time if the ammonium sulphide contains an excess of that element. The analyst must bear in mind that this eliminated sulphur makes the precipitated sulphides appear of a lighter color than they are naturally.

The sulphides corresponding to the metals still remaining in solution are part of them—as those of the alkali and alkali-earth metals—soluble in water; part—as those of aluminium and chromium—decomposed by water into hydroxides and hydrosulphuric acid; part—as those of the fourth group—insoluble in water. These latter would accordingly have been precipitated by hydrosulphuric acid, but for the free acid present. If, therefore, this free acid is removed, *i.e.*, if the solution is made alkaline, and then treated with more hydrosulphuric acid, if required, or, what will answer both purposes at once, if

4. *Ammonium Sulphide*

is added to the solution,* the sulphides of the metals of the fourth group will precipitate: viz., the SULPHIDES OF IRON, MANGANESE, COBALT, NICKEL, and ZINC. But in conjunction with them, ALUMINIUM HYDROXIDE, CHROMIC HYDROXIDE, and CALCIUM PHOSPHATE are thrown down, because the tendency of ammonium to unite with the acid of the aluminium or chromic salt, or for that which keeps the calcium phosphate in solution, causes the elements of the ammonium sulphide to transpose with those of water, thus giving rise to the formation of ammonium hydroxide and of hydrosulphuric acid. The former combines with the acid, the latter escapes, being incapable of entering into combination with the liberated hydroxides or with the calcium phosphate,—the hydroxides and the calcium salt precipitate.

There remain now in solution only the alkali-earth metals and the alkali metals. The normal carbonates of the former are insoluble in water, whilst those of the latter are soluble. If, therefore, we now add

* After previous neutralization of the free acid by ammonia, to prevent unnecessary evolution of hydrosulphuric acid: and after previous addition also, if necessary, of ammonium chloride to prevent the precipitation of magnesium by ammonia.

5. *Ammonium Carbonate,*

together with a little pure ammonia, to guard against the possible formation of bicarbonates, the whole of the alkali-earth metals might be expected to precipitate. This is, however, the case only as regards BARIUM, STRONTIUM, and CALCIUM;* of magnesium, we know that, owing to its disposition to form soluble compounds with ammonium salts, it precipitates only in part; and that the presence of additional ammonium salt will altogether prevent its precipitation, at least within a reasonable space of time. To guard against any uncertainty arising from this cause, ammonium chloride is added previously to the addition of the ammonium carbonate, the mixture soon after filtered, and thus the precipitation of the magnesium is altogether prevented.

We have now still in solution MAGNESIUM and the ALKALI METALS. The detection of magnesium may be effected by means of sodium phosphate and ammonia; but its separation requires a different method, since the presence of phosphoric acid would impede the further progress of the analysis. The process which serves to effect the removal of the magnesium is based upon the insolubility of that earth in the pure state. The substance under examination is accordingly ignited in order to expel the ammonium salts, and the magnesium is then precipitated by means of baryta water, the alkalies, together with the newly formed barium salt and the excess of the baryta added, remaining in solution. By the addition of ammonium carbonate the barium is removed from the solution, which now only contains the alkali metals and ammonium salts. If the ammonium salts are then removed by ignition, the residue consists of the fixed alkali chlorides alone. But as barium carbonate is slightly soluble in ammonium salts, and gives upon evaporation with ammonium chloride, ammonium carbonate, and barium chloride, it is usually necessary, after the expulsion of the ammonium salts by ignition, to precipitate once more with ammonium

* It has been already mentioned in § 99 that traces of these remain in solution partly because their carbonates are not absolutely insoluble in water, but principally because they are notably soluble in ammonium chloride. On account of this deportment we test the filtrate from the ammonium carbonate precipitate with ammonium sulphate and oxalate (164). In the general explanation of the course given in the text, these traces of barium, strontium, and calcium are not taken into account.

carbonate and a few drops of ammonium oxalate, in order to obtain a solution perfectly free from barium.

Lastly, to effect the detection of the AMMONIUM, a fresh portion of the substance must of course be taken.

b. DETECTION OF THE ACIDS.

Before passing on to the examination for acids and acid radicals, the analyst should first ask himself which of these substances may be expected to be present, to judge from the nature of the detected metals and the class to which the substance under examination belongs with respect to its solubility, since this will save him the trouble of unnecessary experiments. Upon this point I refer the student to the table on p. p. 487-489.

The general reagents applied for the detection of the acids are, for the inorganic acids BARIUM CHLORIDE and SILVER NITRATE; for the organic acids, CALCIUM CHLORIDE and FERRIC CHLORIDE. It is therefore indispensable that the analyst should first assure himself whether the substance under examination contains only inorganic acids, or whether the presence of organic acids must also be looked for. The latter is invariably the case if the body, when ignited, turns black, owing to separation of carbon. In the examination for metals the general reagents serve to effect the actual separation of the several groups of metals from each other; but in the examination for acids they serve simply to demonstrate the presence or absence of the acids belonging to the different groups.

Let us suppose we have an aqueous solution containing the whole of the acids, in combination with sodium, for instance.

Barium forms insoluble, or difficultly soluble, compounds with sulphuric acid, phosphoric acid, arsenious acid, arsenic acid, carbonic acid, silicic acid, boric acid, chromic acid, oxalic acid, tartaric acid, and citric acid; barium fluoride also is insoluble, or at least only sparingly soluble; all these compounds are soluble in hydrochloric acid, with the exception of barium sulphate. If, therefore, to a portion of our neutral, or, if necessary, neutralized solution, we add,

1. *Barium Chloride,*

the formation of a precipitate will denote the presence of at least one of these acids. By treating the precipitate with hydrochloric acid we learn at once whether sulphuric acid is present or not, as all the salts of barium being soluble in this menstruum, with the exception of the sulphate, a residue left undissolved by the hydrochloric acid can consist only of the latter salt. Where barium sulphate is present, the reaction with barium chloride fails to lead to the positive detection of the whole of the other acids enumerated; for upon filtering the hydrochloric solution of the precipitate and supersaturating the filtrate with ammonia, the borate, tartrate, citrate, etc., of barium do not always fall down again, being kept in solution by the ammonium chloride formed. For this reason barium chloride cannot serve to effect the actual separation of the whole of the acids named, and, except as regards sulphuric acid, we set no value upon this reagent as a means of effecting their individual detection. Still it is of great importance as a reagent, since the non-formation of a precipitate upon its application in neutral or alkaline solutions proves at once the absence of so considerable a number of acids.

The compounds of silver with sulphur, chlorine, iodine, bromine, cyanogen, ferro- and ferricyanogen, and with phosphoric acid, arsenious acid, arsenic acid, boric acid, chromic acid, silicic acid, oxalic acid, tartaric acid, and citric acid, are insoluble, or difficultly soluble in water. The whole of these compounds are soluble in dilute nitric acid, with the exception of the chloride, iodide, bromide, cyanide, ferrocyanide, ferricyanide, and sulphide of silver. If, therefore, we add to our solution, which, for the reason just now stated, must be perfectly neutral,

2. *Silver Nitrate,*

and precipitation ensues, this shows at once the presence of one or several of the acids enumerated: chromic acid, arsenic acid, and several others, which form colored salts with silver, may be individually recognized with tolerable certainty by the mere color of the precipitate. By treating the precipitate now with nitric acid, we see whether it contains silver

sulphide or any of the haloid compounds of silver, as these remain undissolved, whilst all the other salts dissolve. Silver nitrate fails to effect the complete separation of those acids which form with silver compounds insoluble in water, from the same cause which renders the separation of acids by barium chloride uncertain, viz., the ammonium salt formed prevents the reprecipitation by ammonia of several of the silver salts from the acid solution. Silver nitrate, besides effecting the separation of chlorine, iodine, bromine, cyanogen, etc., and indicating the presence of chromic acid, etc., serves, like barium chloride, to demonstrate at once the absence of a great many acids, where it produces no precipitate in neutral solutions.

The deportment which the solution under examination exhibits with barium chloride and with silver nitrate, indicates therefore at once the further course of the investigation. Thus, for instance, where barium chloride has produced a precipitate, whilst silver nitrate has failed to do so, it is not necessary to test for phosphoric acid, chromic acid, boric acid, silicic acid, arsenious acid, arsenic acid, oxalic acid, tartaric acid, and citric acid, provided always the solution was sufficiently concentrated and did not already contain ammonium salts. The same is the case if we obtain a precipitate by silver nitrate, but none by barium chloride.

Returning now to the supposition which we have made here, viz., that the whole of the acids are present in the solution under examination, the reactions with barium chloride and silver nitrate would accordingly have demonstrated already the presence of SULPHURIC ACID and led to the application of the special tests for CHLORINE, BROMINE, IODINE, CYANOGEN, FERROCYANOGEN, FERRICYANOGEN, and SULPHUR;* and there would be reason to test for all the other acids precipitable by these two reagents. The detection of these acids is based upon the results of a series of special experiments, which have already been fully described and explained in the course of the present work: the same remark applies to the rest of the inorganic acids, accordingly to nitric acid and chloric acid.

Of the ORGANIC ACIDS, oxalic acid, paratartaric acid, and tartaric acid, are precipitated by calcium chloride in the cold, in presence of ammonium chloride; the two former immediately,

* For the separation and special detection of these substances, I refer to § 157.

the latter often only after some time; but the precipitation of calcium citrate is prevented by the presence of ammonium salts, and ensues only upon ebullition or upon mixing the solution with alcohol; the latter agent serves also to effect the separation of calcium malate and succinate from aqueous solutions. If, therefore, we add to our fluid,

3. *Calcium Chloride in excess* and Ammonium Chloride,

OXALIC ACID, PARATARTARIC ACID, and TARTARIC ACID are precipitated, but the calcium salts of several inorganic acids, which have not yet been separated, calcium phosphate, for instance, precipitate along with them. We must therefore select for the individual detection of the precipitated organic acids such reactions only as preclude the possibility of confounding the organic acids with the inorganic acids that are thrown down along with them. For the detection of oxalic acid we select accordingly solution of calcium sulphate, with acetic acid (§ 145); to effect the detection of the tartaric and paratartaric acids, we treat the precipitate produced by calcium chloride with solution of soda, since the calcium salts of these two acids only are soluble in this menstruum in the cold, but insoluble upon ebullition.

Of the organic acids we have now still in solution citric acid and malic acid, succinic acid and benzoic acid, acetic acid and formic acid. CITRIC ACID, MALIC ACID, SUCCINIC ACID precipitate upon addition of alcohol to the fluid filtered from the oxalate, tartrate, etc., of calcium, which still contains an excess of calcium chloride. Sulphate and borate of calcium invariably precipitate along with the malate, citrate, and succinate of calcium, if sulphuric acid and boric acid happen to be present; the analyst must therefore carefully guard against confounding the calcium precipitates of these acids with those of citric acid, malic acid, and succinic acid. The alcohol is now removed by evaporation, and

4. *Ferric Chloride*

added to the perfectly neutral fluid. This reagent precipitates the BENZOIC ACID and the rest of the SUCCINIC ACID as ferric salts, whilst FORMIC ACID and ACETIC ACID remain in solution. The methods which serve to effect the separation of the several

groups from each other, and the reactions on which the individual detection of the various acids is based, have been fully described and explained in the former part of this work.

B. Special Remarks and Additions to the Systematic Course of Analysis.

I will here call attention to several matters which were necessarily passed over in the description of the ordinary course of analysis, and I shall take the present opportunity of explaining how the course may be expanded to meet the detection of the rare metals.

To § 182.

At the commencement of § 182 the analyst is directed to mix neutral or acid aqueous solutions with hydrochloric acid. This should be done drop by drop. If no precipitate forms a few drops are sufficient, since the only object in that case is to acidify the fluid in order to prevent the subsequent precipitation of the metals of the iron group by hydrosulphuric acid. In the case of the formation of a precipitate, some chemists recommend that a fresh portion of the solution should be acidified with nitric acid. However, even leaving the fact out of consideration that nitric acid also produces precipitates in many cases—in a solution of potassio-tartrate of antimony, for instance—I prefer the use of hydrochloric acid, *i.e.*, the complete precipitation by that acid of all that is precipitable by it, for the following reasons: 1. Metals are more readily precipitated by hydrosulphuric acid from solutions acidified with hydrochloric acid, than from those acidified with nitric acid; 2. In cases where the solution contains silver, (mercurous) mercury, or lead, the further analysis is materially facilitated by the total or partial precipitation of these three metals in the form of chlorides; and 3. This latter form is the best adapted for the individual detection of these three metals when present in the same solution. Besides the application of hydrochloric acid saves the necessity of examining whether the mercury, which may be subsequently detected with the other metals of the fifth group, was originally present in the mercurous or mercuric form. That the lead, if present in large proportion, is obtained partly in the form

of a chloride, and partly in the precipitate produced by hydrosulphuric acid in the acid solution, can hardly be thought an objection to the application of this method, as the removal of the larger portion of the lead from the solution, effected at the commencement, will only serve to facilitate the examination for other metals of the fifth and sixth groups.

As already remarked, a basic antimonious salt may separate from potassio-tartrate of antimony, for instance, or from some other analogous compound, and precipitate along with the insoluble silver chloride and mercurous chloride, and the sparingly soluble chloride of lead. This precipitate, however, is readily soluble in the excess of hydrochloric acid which is subsequently added, and exercises therefore no influence whatever upon the further process. The application of heat to the fluid mixed with hydrochloric acid is neither necessary nor even advisable, since it might cause the conversion of a little of the precipitated mercurous chloride into mercuric chloride.

Should bismuth, antimony, or metastannic acid be present, the additions of the washings of the precipitate produced by hydrochloric acid to the first filtrate will cause turbidity. The turbidity is occasioned, in the case of bismuth and antimony, by the insufficiency of the free hydrochloric acid present to prevent the separation of basic salt; in the case of metastannic acid, by the metastannic chloride being first precipitated, then redissolving in the wash-water, and then meeting with hydrochloric acid in the filtrate. This turbidity exercises, however, no influence upon the further process, since hydrosulphuric acid as readily converts these finely divided precipitates into sulphides as if the metals were in actual solution.

In the case of alkaline solutions, the addition of hydrochloric acid must be continued until the fluid shows a strongly acid reaction. The substance which causes the alkaline reaction combines with the hydrochloric acid, and the bodies originally dissolved in that alkaline substance separate. Thus, if the alkali is present in the free state, zinc hydroxide, for instance, may precipitate. But these hydroxides will redissolve in an excess of hydrochloric acid, whereas silver chloride will not redissolve, and lead chloride with difficulty. If a metallic sulphur salt is the cause of the alkaline reaction, the

sulphur acid, *e.g.*, antimonious sulphide, precipitates upon the addition of the hydrochloric acid, whilst the sulphur base, *e.g.*, sodium sulphide, transposes with the constituents of the hydrochloric acid, forming sodium chloride and hydrosulphuric acid. If a carbonate, a cyanide, or a sulphide of an alkali metal is the cause of the alkaline reaction, carbonic acid, or hydrocyanic acid, or hydrosulphuric acid escapes. All these phenomena should be carefully observed by the analyst, since they not only indicate the presence of certain substances, but demonstrate also the absence of entire groups of bodies.

Precipitates are produced also by hydrochloric acid in solutions containing thallium, alkali salts of antimonic acid, tantalic acid, niobic acid, molybdic acid and tungstic acid. The antimonic, tantalic, and molybdic precipitates dissolve (the tantalic acid precipitate to an opalescent fluid), whilst the CHLORIDE OF THALLIUM, NIOBIC ACID, and TUNGSTIC ACID do not dissolve in excess of hydrochloric acid. The latter therefore remain with the precipitate, which may also contain silver chloride, mercurous chloride, lead chloride, and silicic acid. Separation of sulphur ensuing after some time on addition of hydrochloric acid, accompanied by the odor of sulphurous acid, indicates THIOSULPHURIC (HYPOSULPHUROUS) ACID. If you have cause to test for rare metals, after exhausting the precipitate with boiling water, examine the fluid for THALLIUM by potassium iodide (confirming by the spectroscope). On exhausting again with ammonia to dissolve out the silver chloride, and treating the residue with nitric acid, the niobic, tungstic and silicic acids will remain behind. The two first may be separated from the latter by fusing with sodium disulphate, treating with water, and finally with dilute solution of ammonium carbonate. They may be separated from each other by treating the solution with excess of ammonium sulphide.

To §§ 183 and 184.

A judicious distribution and economy of time is especially to be studied in the practice af analysis; many of the operations may be carried on simultaneously, which the student may readily perceive and arrange for himself. For instance, after throwing the hydrosulphuric acid precipitate on the filter, you may test the first drops of the filtrate with ammonium sulphide to see if there is any metal of that group present, and if this is not the case you may proceed to test with ammonium carbonate. You will thus be able, while washing the hydrosulphuric acid precipitate, to throw down the filtrate with the proper group-test. Again, while you are treating

the first precipitate with ammonium sulphide you may wash the second precipitate.

In cases where the analyst has simply to deal with metals of the sixth group (*e.g.*, antimony) and of the fourth or fifth group (*e.g.*, iron or bismuth), he need not precipitate the acidified solution with hydrosulphuric acid, but may, after neutralization, at once add ammonium sulphide in excess. The iron, etc., will in that case precipitate, whilst the antimony, etc., will remain in solution, from which they will, by addition of an acid, at once be thrown down as antimonious sulphide, etc. This method has the advantage that the fluid is diluted less than in the case where solution of hydrosulphuric acid is employed, and that the operation is performed more expeditiously and conveniently than is the case where hydrosulphuric acid gas is conducted into the fluid. I must again call attention to the very constant occurrence of mistakes through the use of spoilt hydrosulphuric acid water, through the use of an insufficient quantity of good hydrosulphuric acid water, or through passing the gas into a solution containing a too large excess of hydrochloric or nitric acid. Imagine a very acid solution containing iron and bismuth; if you pass hydrosulphuric acid gas, or add a few drops of the water, no precipitate will be produced; and if in the idea that no metal of the hydrosulphuric acid group is present, you then add ammonium sulphide, you will obtain a precipitate containing the sulphides of iron and bismuth; and on treating this with dilute hydrochloric acid, the bismuth sulphide will remain as a black residue, indicating the presence of nickel or cobalt. In this case you should have either diluted the fluid considerably before passing the gas, or added a large quantity of hydrosulphuric acid water, when the bismuth would have been precipitated in its proper place. Again, arsenic acid may be easily missed if the action of the hydrosulphuric acid is not supplemented by heat.

If the hydrosulphuric acid precipitate is not well washed, on warming it with nitric acid the mercuric sulphide may dissolve from the presence of hydrochloric acid, and on testing the action of ammonium sulphide the results will not be trustworthy.

It happens occasionally that in treating acid solutions with hydrosulphuric acid, or in decomposing by hydrochloric acid

the ammonium sulphide used to effect the solution of sulphides of the sixth group that may be present, precipitates are obtained which look almost like pure sulphur, and thus leave the analyst in doubt whether it is really requisite to examine them for metals. In such cases the precipitate may be first washed, then dried, and treated finally with carbon disulphide to remove the sulphur; this will show whether or not a trifling quantity of a sulphide is mixed with the sulphur.

The following sulphides of the rarer elements pass into the precipitate produced by hydrosulphuric acid in an acid solution; the sulphides of palladium, rhodium, osmium, ruthenium, iridium,* molybdenum, tellurium, selenium, and possibly of thallium.†

The following rare compounds cause separation of sulphur, by decomposing the hydrosulphuric acid: the higher oxides and chlorides of manganese and cobalt, vanadic acid (with blue coloration of the fluid), nitrous acid, sulphurous acid, thiosulphuric (hyposulphurous) acid, hypochlorous and chlorous acids, bromic acid and iodic acid.

On treating the precipitate with ammonium sulphide the sulphides of iridium, molybdenum, tellurium, and selenium dissolve, whilst the sulphides of palladium, rhodium, osmium, and ruthenium, and of thallium, remain undissolved.

To § 185.

If a precipitate containing all the sulphides of the sixth group, precipitable by hydrosulphuric acid, from acid solution (of tin, antimony, arsenic, tellurium, selenium, molybdenum, gold, platinum, and iridium), is fused, according to § 185 with sodium carbonate and nitrate, and the fused mass treated with cold water, the TELLURIC ACID, SELENIC ACID, and MOLYBDIC ACID dissolve with the arsenic acid, whilst the IRIDIUM is left undissolved with the stannic oxide, sodium antimonate, gold, and platinum.

For the way of detecting the rare elements in the solution and in the precipitate, see § 185.

To § 186.

Besides the methods described in the systematic course, to separate cadmium, copper, lead, and bismuth, the following process will also be found to give highly satisfactory results: Add sodium carbonate to the nitric acid solution as long as a

* The metals of the platinum ores are precipitated with difficulty by hydrosulphuric acid. To attain the end in view, hydrosulphuric acid gas must be perseveringly conducted into the fluid, and heat applied at the same time.

† Tungsten and vanadium are not found in the precipitate thrown down from an acid solution by hydrosulphuric acid. They can be present only where the fluid has first been mixed with ammonium sulphide, then with acid in excess; but in that case the sulphides of nickel and cobalt will also be found with those of the fifth and sixth groups. Thallium, although it is not precipitated from acid solutions by hydrosulphuric acid under ordinary circumstances, may be thrown down in connection with arsenious sulphide.

precipitate continues to form, then solution of potassium cyanide in excess, and heat gently. This effects the complete separation of lead and bismuth in the form of carbonates, whilst copper and cadmium are obtained in solution in the form of copper potassium cyanide and cadmium potassium cyanide. Lead and bismuth may now be readily separated from one another by means of sulphuric acid. The separation of the copper from the cadmium is effected by adding to the solution of the cyanides of these two metals in potassium cyanide, hydrosulphuric acid in excess, gently heating, and then adding some more potassium cyanide, in order to redissolve the copper sulphide which may have precipitated along with the cadmium sulphide. A residuary yellow precipitate (cadmium sulphide), insoluble in the potassium cyanide, demonstrates the presence of cadmium. Filter the fluid from this precipitate, and add hydrochloric acid to the filtrate, when the formation of a black precipitate (cupric sulphide) will demonstrate the presence of copper.

Where there is reason to suppose that the precipitate containing the sulphides of the fifth group contains also the sulphides of palladium, rhodium, osmium, ruthenium, or thallium, first test a portion in the spectroscope for thallium, and then proceed as follows:

Fuse the precipitate with potassium hydroxide and chlorate, heat ultimately to redness, let cool, then treat the mass with water. The solution contains potassium osmate and ruthenate, which latter imparts a deep yellow color to it. If the fluid is cautiously neutralized with nitric acid, BLACK RUTHENIOUS OXIDE separates; if more nitric acid is added to the filtrate, and the fluid then distilled, OSMIUM TETROXIDE passes over. If the residue left upon the extraction of the fused mass with water is gently ignited in hydrogen gas,* then cautiously treated with dilute nitric acid, the copper, lead, etc., are dissolved, whilst the rhodium and palladium are left undissolved. The PALLADIUM may then be dissolved out of the residue by means of aqua regia, leaving the RHODIUM undissolved. For the further examination of the isolated metals, I refer to § 124. A separate portion of the precipitate of the sulphides must be examined for mercury, in the event of the above process being adopted.

To § 187.

Assuming all elements not yet precipitated to be present in the fluid filtered from the precipitate produced in an acid solution by hydrosulphuric acid, the precipitate produced by addition of ammonium chloride to this filtrate, neutralization with ammonia, and addition of ammonium sulphide in excess, will contain the following elements:

* Cadmium may escape in this operation.

a. In the form of sulphides : cobalt, nickel, manganese, iron, zinc, uranium, thallium, indium.

b. In the form of hydroxides : aluminium, beryllium, thorium, zirconium, yttrium, erbium, cerium, lanthanium, didymium, chromium, titanium, tantalum, niobium.*

Where there is reason to suspect the presence of some of the rare elements in the precipitate, the following method may be recommended as the most suitable in many cases :

1. Dry the greater part of the washed precipitate, ignite in a porcelain crucible, then fuse perseveringly in a platinum crucible with *potassium disulphate;* let the fused mass cool, soak in cold water and digest for some time without application of heat. Filter the solution from the residue.

The RESIDUE, which contains the acids of tantalum and niobium, and may contain also silicic acid and a little undissolved ferric oxide and chromic oxide, gives, on fusion with sodium hydroxide and some sodium nitrate, a mass out of which dilute solution of soda will dissolve chromate and silicate of sodium, leaving undissolved, with the ferric oxide, sodium tantalate and niobate (being insoluble in solution of soda). After removing the excess of soda, treat repeatedly with a very dilute solution of sodium carbonate, in which the SODIUM NIOBATE dissolves much more readily than the TANTALATE. For the further examination compare § 104, 10 and 11.

Treat the SOLUTION, which contains all the other bases, etc., of the third and fourth groups, with hydrosulphuric acid, to reduce the ferric salts, dilute considerably, heat to boiling and keep boiling for some time, whilst conducting carbon dioxide into the fluid. If a precipitate is formed, examine this for TITANIC OXIDE ; it may contain also a little ZIRCONIUM.

Concentrate the filtrate by evaporation, with addition of some nitric acid ; precipitate with *ammonia*, filter, and wash ; redissolve the washed precipitate in hydrochloric acid, and precipitate again with ammonia. This will give almost the whole of the ZINC, MANGANESE, NICKEL, and COBALT in solution, whilst the earths are left undissolved with the hydroxides of iron, indium, uranium, and chromium. Redissolve the precipitate in hydrochloric acid, and add *concentrated solution of potassa*, without applying heat. This will leave in solution the chromic hydroxide, the alumina, and the berylla, whilst precipitating the other earths with the hydroxides of iron, indium and uranium. Dilute the alkaline solution, and boil some time ; this will throw down the berylla and the chromic hydroxide, leaving the ALUMINIUM in solution. The latter may then be precipitated by ammonium chloride. Fuse the precipitate of berylla and chromic hydroxide with sodium carbonate and potassium chlorate, and separate the BERYLLA from the CHROMIC ACID in the same way in which the separation of alumina from chromic acid is effected (§ 103).

The precipitate, which contains the hydroxides of iron, indium, and uranium, and the earths insoluble in potassa, may also contain chromic hydroxide, and under certain circumstances, *e.g.*, in presence of yttria and cerium sesquioxide, also alumina and berylla. Dissolve it in hydrochloric acid, remove an overlarge excess of the acid by evaporation, dilute, add *barium carbonate*, and let the mixture stand six hours in the cold.

The precipitate produced contains the IRON, INDIUM, and URANIUM (also

* Of niobic acid only the trifling traces redissolved on the precipitation by hydrochloric acid can be present here.

THORIUM and a part of the CERIUM * ?) and possibly some aluminium and chromium. Separate uranium in a portion of the precipitate by redissolving in hydrochloric acid, and adding excess of sodium bicarbonate. Test another portion in the spectroscope for INDIUM, and another by fusing with sodium carbonate and potassium chlorate for CHROMIUM.

To the filtrate from the barium carbonate precipitate first add sulphuric acid to remove barium, filter, concentrate strongly by evaporation, neutralise exactly with potassa (leaving the reaction rather acid than alkaline), add *normal potassium sulphate* in crystals, boil, and let the fluid stand twelve hours. Then filter, and wash with a solution of potassium sulphate. The filtrate contains that portion of the beryllium which may have escaped solution by potassa, also yttrium and erbium. These are precipitated by ammonia, and may then easily be separated by treating with a concentrated warm solution of *oxalic acid*, in which the BERYLLA is soluble, whilst the oxalates of YTTRIUM and of ERBIUM are left undissolved. Now boil the precipitate of the double sulphates repeatedly in water, with addition of some hydrochloric acid, which will dissolve THORIUM (?) CERIUM,* LANTHANIUM, and DIDYMIUM, leaving the sulphate of ZIRCONIUM and potassium undissolved. Thorium and cerium may then be precipitated from the solution by ammonia, and tested by the reactions described in § 104.

2. Test a portion of the remainder of the precipitate in the spectroscope for THALLIUM (and also indium). To be more sure about thallium, dissolve a portion of the precipitate in boiling dilute hydrochloric acid, treat with sulphurous acid till ferric salts are reduced, nearly neutralize with ammonia, and then test with potassium iodide. The precipitate must, under all circumstances, be further examined in the spectroscope.

To §§ 188–191.

The fluid filtered from the precipitate produced by ammonium sulphide may not only contain the alkali earth and the alkali metals, but some nickel and also vanadium and that portion of the tungsten which has been left unprecipitated by hydrochloric acid. The nickel, the vanadium, and the tungsten are present as sulphides dissolved in the excess of ammonium sulphide ; they are thrown down in that form by just acidifying the fluid with hydrochloric acid. Filter the precipitate, wash, dry, fuse with sodium carbonate and nitrate, and treat the fused mass with water; this will dissolve sodium vanadate and tungstate, leaving nickel hydroxide. From this solution the vanadic acid may be separated by means of solid ammonium chloride, the tungstic acid by evaporating with hydrochloric acid and treating the residue with water. The two acids may then be examined as directed § 113, *d*, and § 135, *c*.

For the detection of lithium, cæsium and rubidium, I refer to the analysis of mineral waters (**203** and **204**).

To § 196.

If the rare elements are taken into account, the number of bodies which may remain undissolved on treating a substance with water, hydrochloric acid,

* [Thorium is completely, and cerium partly (slowly) thrown down by *barium carbonate* in the cold. See also zirconium, lanthanium, and didymium, § 104.—ED.]

nitric acid, and aqua regia, is much enlarged. The following bodies, more especially, are either generally, or in the ignited state, or in certain combinations, insoluble or slowly and sparingly soluble in acids;

Berylla, thoria, and zirconia, cerium sesquioxide, titanic oxide, tantalic oxide, niobic oxide, molybdic oxide, tungstic oxide, rhodium, iridium, osmio-iridium, ruthenium.

When you have, in the systematic course of analysis, arrived at **152**, fuse the substance, free from silver, lead, and sulphur, with sodium carbonate and some nitrate, extract the fused mass repeatedly with hot water, and, if a residue is left, fuse this a long time, in a silver crucible, with potassium hydroxide and nitrate and again treat the fused mass repeatedly with water. The alkaline solutions, which may be examined separately or together, may contain beryllium, a portion of the titanic acid, tantalic acid, niobic acid, molybdic acid, tungstic acid, osmic and ruthenic acids, and a portion of the iridium.

If the residue left undissolved by the preceding operation is fused with potassium disulphate, and the fused mass treated with water, the thorium, zirconium, cerium, lanthanium, and didymium, the remainder of the titanium and the rhodium will dissolve. A residue left by this operation may consist of platinum ore metals, and had best be mixed with sodium chloride, and ignited in a stream of chlorine.

With respect to the separation and detection of the several elements that have passed into the different solutions, the requisite directions and instructions have been given in the third section of Part I., and in the additional remarks to §§ 182–191.

To § 197.

The analysis of cyanogen compounds is not very easy in certain cases, and it is sometimes a difficult task even to ascertain whether we have really a cyanide before us or not. However, if the reactions of the substance upon ignition (**8**) be carefully observed, and also whether upon boiling with hydrochloric acid any odor of hydrocyanic acid is emitted (**35**), the presence or absence of a cyanide will generally not remain a matter of doubt.

It must above all be borne in mind that the insoluble cyanogen compounds, occurring in pharmacy, etc., belong to two distinct classes, viz., they are either SIMPLE CYANIDES, or COMPOUNDS OF METALS WITH FERROCYANOGEN or some other analogous radical.

All the simple cyanides are decomposed by boiling with concentrated hydrochloric acid into metallic chlorides and hydrocyanic acid. Their analysis is therefore never difficult. But the ferrocyanides, etc., to which indeed the method described § 197 more exclusively refers, suffer by acids such complicated decompositions that their analysis by means of

acids is a task not so easily accomplished. Their decomposition by potassa or soda is far more simple. The alkali yields its hydroxyl to the metal combined with the ferrocyanogen, etc., the hydroxide thus formed precipitates, and the potassium or sodium forms with the liberated radical soluble ferrocyanide, etc., of potassium or sodium. But several hydroxides are soluble in an excess of potassa, as, *e.g.*, those of lead, zinc, etc. If, therefore, the zinc-potassium ferrocyanide, for instance, is boiled with solution of caustic potassa, it dissolves completely, and we may assume that the solution contains potassium ferrocyanide and zinc hydroxide dissolved in potassa. Were we to add an acid to this solution, we should of course simply reobtain the original precipitate of zinc-potassium ferrocyanide, and the experiment would consequently be of no avail. To prevent this failure, we conduct hydrosulphuric acid into the solution in potassa, but only until the precipitable metals are completely thrown down, and not until the solution smells of sulphuretted hydrogen. This serves to convert into sulphides all the heavy metals which the potassa holds in solution as hydroxides. Those sulphides which are insoluble in potassa, those of lead, zinc, etc., precipitate, whilst those which are soluble in alkali sulphides, such as stannic sulphide, antimonious sulphide, etc., remain in solution. To effect the detection of these also, the fluid is now acidified, and, if necessary, more hydrosulphuric acid conducted into it.

In the filtrate from the hydroxides and sulphides we have still those metals which form radicals with cyanogen, and also aluminium, which has dissolved in the original treatment with potassa, and would not have been separated. Finally also the other acids must be tested for here. It is therefore directed to divide the solution into two parts, and to test one for acids, the other for aluminium and those metals which form radicals with cyanogen. The prescribed heating of this second part with concentrated sulphuric acid has the effect of decomposing the cyanogen compounds, and converting the metals into sulphates which remain behind (H. Rose*).

If you simply wish to examine for bases in simple or compound cyanides, and for that purpose to destroy the cyanogen compound, it will suffice to heat the powdered substance

* Zeitschr. f. anal. Chem. 1, 194.

in a platinum dish with concentrated sulphuric acid diluted with a little water, till almost all the free acid is driven off. The residue will consist of sulphates which are to be dissolved in hydrochloric acid and water.

The reason why ferrocyanides and similar compounds which have been fully washed with water, require to be tested for alkalies is because alkali ferrocyanides, etc., are often precipitated along with insoluble ferrocyanides, etc., and cannot be removed by washing.

APPENDIX.

I.

Deportment of the most important Medicinal Alkaloids with Reagents, and Systematic Method of effecting their Detection.

§ 222.

The detection and separation of the alkaloids is far more difficult than the detection and separation of the inorganic bases. In many cases the combinations in which an alkaloid can be separated from others are not sufficiently insoluble to allow of complete separation, in other cases we only know the outward appearance of a reaction and not its cause, and are consequently ignorant of the conditions which may determine or modify it; again, many alkaloids are as yet not known to have any characteristic reaction whatever.

However, in the following pages the subjects will be treated as thoroughly as our knowledge will allow, the more commonly occurring alkaloids being included, viz., nicotin, conin, morphin, narcotin, quinin, cinchonin, strychnin, brucin, veratrin, and atropin.

This appendix will be divided into the following sections:

A. General reagents for the alkaloids.

B. Properties and reactions of the individual alkaloids, arranged in groups. (In this section certain non-nitrogenous bodies are included which are allied to the alkaloids as poisons or are employed in their adulteration, namely, salicin, digitalin, and picrotoxin.)

C. Systematic course for the detection of an alkaloid when only one is present.

D. Systematic course for the detection of alkaloids when several may be present.

E. Detection of alkaloids in the presence of other organic substances.

A. General Reagents for the Alkaloids.

§ 223.

By general reagents for the alkaloids I mean reagents by which they are all or nearly all precipitated. These are well suited to test generally for the presence of an alkaloid in a fluid, and may serve to separate alkaloids from their solutions, but they cannot be employed to distinguish individual alkaloids except in a subordinate degree.

These reagents are as follows: hydrochloroplatinic acid, a solution of iodine in potassium iodide (Wagner*), mercuric potassium iodide (v. Planta†), cadmium-potassium iodide (Marme‡), bismuth-potassium iodide (Dragendorff§), phosphomolybdic acid (de Vrij, Sonnenschein‖), phosphoantimonic acid (Fr. Schulze¶), metatungstic acid (Scheibler**), picric acid (H. Hager††).

Hydrochloroplatinic acid forms with the hydrochlorides of the alkaloids compounds analogous to ammonium platinichloride. Some of these compounds are difficultly soluble in water, some are rather easily soluble. They are best obtained and most completely separated by mixing the solutions with a sufficient quantity of hydrochloroplatinic acid, evaporating nearly to dryness and treating with alcohol. They have a yellow color of various shades, some are crystalline, some flocculent, and in general they are more soluble in hydrochloric acid than in water.

A solution of iodine in potassium iodide (containing 12.7 grm. free iodine in 1 litre) precipitates the solutions of the salts of all the alkaloids. The precipitates are brown and flocculent. Their formation and separation is assisted by acidifying with sulphuric acid. By washing the precipitate, dissolving it in solution of sulphurous acid and evaporating on the water bath to remove the excess of sulphurous acid

* Zeitschr. f. anal. Chem., 4, 387.
† Verhalten der wichtigsten Alkaloide gegen Reagentien, Heidelberg, 1846.
‡ Zeitschr. f. anal. Chem., 6, 123.
§ *Ib.*, 5, 406.
‖ Ann. d. Chem. u. Pharm., 104, 47.
¶ *Ib.*, 109, 179.
** Journ. f. prakt. Chem., 80, 211.
†† Pharm. Centralhalle, 10r Jahrg., 131.

and the hydriodic acid, the alkaloid will remain in combination with sulphuric acid. If the precipitate was separated from a fluid containing a quantity of other organic substances, before proceeding as just stated, dissolve it in a dilute solution of sodium thiosulphate (hyposulphite), filter, and re-precipitate with iodine solution.*

MERCURIC POTASSIUM IODIDE precipitates the solutions of the salts of the alkaloids. The precipitates are white or yellowish white, insoluble in water and dilute hydrochloric acid.

CADMIUM-POTASSIUM iodide † precipitates the solutions of salts of the alkaloids after acidification with sulphuric acid, even when very dilute. The precipitates are at first all flocculent and white, some of them soon become crystalline. They are insoluble in ether, readily soluble in alcohol, less soluble in water, readily soluble in excess of the precipitant. They have a tendency to decompose by long standing. The alkaloids may be obtained from the undecomposed precipitates by mixing with an alkali carbonate or hydroxide and water, and shaking with benzol, amylic alcohol, ether, or the like.

BISMUTH-POTASSIUM IODIDE ‡ added drop by drop to solutions of salts of the alkaloids acidified with sulphuric acid (10 c.c. of the alkaloid solution and five drops of concentrated sulphuric acid) produces almost immediately flocculent orange precipitates in the case of nicotin, conin, morphin, narcotin, quinin, cinchonin, strychnin, brucin, atropin, and most other alkaloids; veratrin, on the other hand, gives only a faint turbidity. The precipitates formed with the first-named alkaloids agglutinate together to some extent when heated; they dissolve by long continued boiling, and separate again for the

* By dissolving the brownish-red precipitate produced by mixing the iodine solution with a salt of strychnin in alcohol containing sulphuric acid, and evaporating, prismatic crystals of a strong polarizing power will be obtained (DE VRIJ and VAN DER BURG. Jahresber. von LIEBIG u. KOPP, 1857, 602). Until the optical properties of the analogous compounds of the other alkaloids shall have been examined, we are unable to state whether this reaction is characteristic or not.

† Prepared by saturating a boiling concentrated solution of potassium iodide with cadmium iodide, and adding an equal volume of cold saturated solution of potassium iodide. The concentrated solution keeps well, but not the dilute.

‡ Prepared as follows:—Heat 32 parts of bismuth sulphide in a combustion tube sealed at one end, with 41.5 parts of iodine, collect the bismuth iodide in a receiver, purify it by resublimation, heat it with solution of potassium iodide, filter hot, and add to the solution an equal volume of a cold saturated solution of potassium iodide. The concentrated solution keeps well, but not the dilute. On mixing 10 c.c. water with 5 drops of concentrated sulphuric acid and adding 1 or 2 drops of the reagent, no turbidity should occur.

most part on cooling. None of the precipitates are crystalline. The alkaloids may be separated from the precipitates as given under the previous reagent.

PHOSPHOMOLYBDIC ACID* is precipitated by the solutions of all alkaloids, even when their quantity is very minute. The precipitates are light yellow, ochreous or brownish yellow, insoluble or difficultly soluble at the ordinary temperature in water, alcohol, ether, and dilute mineral acids, with the exception of phosphoric acid; they are most insoluble in dilute nitric acid, especially when it contains some of the reagent; acetic acid also is almost without action in the cold, but in the heat it has a solvent action. The precipitates dissolve in the hydroxides and carbonates of the alkali metals, generally with ease and with separation of the alkaloids. The latter may be removed by shaking with ether, amylic alcohol, benzol, or the like.

PHOSPHOANTIMONIC ACID, obtained by dropping antimonic chloride into aqueous phosphoric acid, also precipitates ammonia and most of the alkaloids (not caffein). The reactions are delicate, but they are generally less delicate than with the last reagent, especially in the case of nicotin and conin; this reagent is more delicate in one single instance, namely, for atropin. The precipitates are usually flocculent and whitish, the brucin precipitate is rose-colored. On heating it dissolves, on cooling it separates again from the fluid, which remains colored intensely carmine.

METATUNGSTIC ACID† precipitates the solutions of all the alkaloids. The precipitates are white and flocculent. The delicacy of the reactions is extreme. Acid solutions containing only one part of quinin or strychnin in 200,000 are rendered distinctly turbid, and deposit minute flocks in 24 hours.

PICRIC ACID precipitates almost all the alkaloids, even from solutions containing a large excess of sulphuric acid. The precipitates are yellow, and insoluble in excess of the pre-

* Prepared as follows:—Precipitate the nitric acid solution of ammonium molybdate with sodium phosphate, wash the precipitate well, suspend it in water, and warm with addition of sodium carbonate to complete solution. Evaporate to dryness, ignite the residue, and if reduction has taken place, moisten with nitric acid, and ignite again. Warm with water, and dissolve by adding nitric acid in considerable excess. One part of the residue should make 10 parts of solution. The solution must be protected from ammoniacal fumes.

† Instead of the pure acid you may use a metatungstate acidified with mineral acid, or even ordinary sodium tungstate, with addition of phosphoric acid. Phosphoric acid, when added to an ordinary soluble tungstate, removes part of the base, and so produces a metatungstate.

cipitant; they are usually formed even in very dilute solutions. Morphin and atropin (pure) are only thrown down from neutral and concentrated solutions; the precipitates disappear on dilution (caffein and pseudomorphin are not precipitated, likewise the glucosides).

B. Properties and Reactions of the individual Alkaloids.

I. Volatile Alkaloids.

The volatile alkaloids are fluid at the common temperature, and may be volatilized in the pure state as well as when mixed with water. They are accordingly obtained in the distillate when their salts are distilled with strong fixed bases and water. Their vapors, when brought in contact with those of volatile acids, form a white cloud.

1. Nicotin ($C_{10} H_{14} N_2$).

§ 224.

1. Nicotin occurs in the leaves and seed of tobacco. In its pure state, it forms a colorless, oily liquid, of 1.048 sp. gr.; the action of air imparts a yellowish or brownish tint to it. It boils at 250°, suffering, however, partial decomposition in the process; but, when heated in a stream of hydrogen gas, it distils over unaltered, between 100° and 200°. It dissolves with ease in water, alcohol, and ether.

Nicotin has a peculiar, disagreeable, somewhat ethereal, tobacco-like odor. On heating it gives off a very powerful odor of tobacco. It has an acrid, pungent taste, and very poisonous properties. Dropped on paper, it makes a transparent stain, which slowly disappears; it turns turmeric paper brown, and litmus paper blue. Concentrated aqueous solution of nicotin shows these reactions more distinctly than the alkaloid in the pure state.

2. Nicotin has the character of a pretty strong base; it precipitates metals as hydroxides from their solutions, and forms salts with acids. The salts of nicotin are non-volatile, freely soluble in water and alcohol, insoluble in ether and amylic alcohol; they are inodorous, but taste strongly of tobacco; part of them are crystallizable. Their solutions,

when distilled with solution of potassa, give a distillate containing nicotin. By neutralizing this with oxalic acid, and evaporating, nicotin oxalate is produced, which may be freed from any admixture of ammonium oxalate, by means of alcohol, in which the former salt is soluble, the latter insoluble.

3. If an aqueous solution of nicotin, or a solution of a nicotin salt mixed with solution of soda or potassa, is shaken with *ether*, the nicotin is dissolved by the ether; if the latter is then allowed to evaporate on a watch glass at 20° or 30°, the nicotin remains behind in drops and streaks; on warming the watch glass, it volatilizes in white fumes of strong odor.

4. *Hydrochlorcplatinic acid* produces in aqueous solutions of nicotin or its salts whitish-yellow flocculent precipitates. On heating the fluid containing the precipitate, the latter dissolves, but upon continued application of heat it very speedily separates again in form of an orange-yellow, crystalline, heavy powder, which, under the microscope, appears to be composed of roundish crystalline grains. If a rather dilute solution of nicotin, supersaturated with hydrochloric acid, is mixed with hydrochloroplatinic acid, the fluid at first remains clear; after some time, however, the salt separates in small crystals (oblique four-sided prisms), clearly discernible with the naked eye.

5. *Hydrochlorauric acid* added in excess to aqueous solutions of the alkaloid or its salts produces a reddish-yellow flocculent precipitate, sparingly soluble in hydrochloric acid.

6. Solution of *iodine in potassium iodide* and water, when added in small quantity to an aqueous solution of nicotin, produces a yellow precipitate, which after a time disappears. Upon further addition of iodine solution, a copious kermes-colored precipitate separates; but this also disappears again after a time. Solutions of the salts are precipitated with a kermes-brown color.

7. Solution of *tannic acid* produces in aqueous solution of nicotin a copious white precipitate, which redissolves upon addition of hydrochloric acid.

8. If an aqueous solution of nicotin is added to excess of solution of *mercuric chloride*, an abundant, flocculent, white precipitate is formed. If solution of ammonium chloride is now added to the mixture in sufficient quantity, the entire

precipitate, or the greater part of it, redissolves. But the fluid very soon turns turbid, and deposits a heavy white precipitate.

2. Conin ($C_8 H_{15} N$).

§ 225.

1. Conin occurs in the leaves, seed, and flowers of the spotted hemlock. It forms a colorless oily liquid of .88 sp. gr.; the action of the air imparts to it a brown tint. In the pure state it boils at 168°; when heated in a stream of hydrogen gas, it distils over unaltered; but when distilled in vessels containing air, it turns brown and suffers partial decomposition; with aqueous vapors it distils over freely. It dissolves sparingly in water, 100 parts of water of the common temperature dissolving 1 part of conin. The solution turns turbid on warming, clear again on cooling. Conin is miscible in all proportions with alcohol and ether. The aqueous and alcoholic solutions manifest strong alkaline reaction. Conin has a very strong, pungent, repulsive odor, which affects the head, a most acrid and disagreeable taste, and very poisonous properties.

2. Conin is a strong base; it accordingly precipitates metallic salts in a similar way to ammonia, and forms salts with acids. The salts of conin are soluble in water and in alcohol, ether also dissolves several of them (*e.g.*, the sulphate) to some extent. Conin hydrochloride crystallizes readily; the smallest quantity of conin brought in contact with a trace of hydrochloric acid, yields almost immediately a corresponding quantity of non-deliquescent rhombic crystals (T. H. Wertheim). The sulphate does not crystallize except on very long standing.* The solutions of the salts turn brownish upon evaporation, with partial decomposition of the conin. The dry salts do not smell of the alkaloid; when moistened they smell only feebly of it, but upon addition of soda solution, they at once emit a strong odor. When conin salts are distilled with soda solution, the distillate contains conin. On neutralizing this with oxalic acid, evaporating to dryness, and treating the residue with alcohol, conin oxalate is dissolved, whilst any ammonium oxalate that may be present is left un-

* Zeitschr. f. anal. Chem., 1, 397.

dissolved. As conin is only sparingly soluble in water, and dissolves with still greater difficulty in solution of alkalies, a concentrated solution of a conin salt turns milky upon addition of solution of soda. The minute drops which separate unite gradually, and collect on the surface.

3. If an aqueous solution of a salt of conin is shaken with *soda solution* and *ether*, the conin is dissolved by the ether. If the latter is then allowed to evaporate on a watch glass at 20° or 30°, the conin is left in yellowish colored oily drops.

4. *Hydrochlorauric acid* produces in solutions of the alkaloid or its salts a yellowish-white precipitate, insoluble in hydrochloric acid. *Mercuric chloride* gives with conin a copious white precipitate, soluble in hydrochloric acid. *Hydrochloroplatinic acid* does not precipitate rather dilute aqueous solutions of conin salts, the conin compound corresponding to ammonium platinichloride being insoluble in spirits of wine and ether, but tolerably soluble in water. The salt also dissolves by boiling with alcohol; it separates in the amorphous form on cooling.

5. To solution of *iodine in potassium iodide* and water, and to solution of *tannic acid*, conin comports itself like nicotin.

6. *Chlorine water* produces in a mixture of water and conin a strong, white turbidity.

The volatile alkaloids are most easily recognized when pure; the great object of the analyst must accordingly be to obtain them in that state. The way of effecting this is the same for nicotin as for conin, and has already been given in the foregoing paragraph, viz., to distil with addition of soda solution, neutralize with oxalic acid, evaporate, dissolve in alcohol, evaporate the solution, treat the residue with water, add soda solution, shake the mixture with ether, and let the latter evaporate spontaneously. Conin is distinguished from nicotin chiefly by its odor, its sparing solubility in water, and its behavior with chlorine water.

II. Non-volatile Alkaloids.

The non-volatile alkaloids are solid, and cannot be distilled over with water.

FIRST GROUP.

NON-VOLATILE ALKALOIDS WHICH ARE PRECIPITATED BY POTASSA OR SODA FROM THE SOLUTIONS OF THEIR SALTS, AND REDISSOLVE READILY IN AN EXCESS OF THE PRECIPITANT.

Of the alkaloids of which I purpose to treat here, one only belongs to this group, viz.,

MORPHIN ($C_{17} H_{10} N O_3 = \dot{M}o$).

§ 226.

1. Morphin occurs with the alkaloids codein, thebain, papaverin, narcotin, and narcein, and with meconic acid and meconin, in opium, the dried milky juice of the green capsules of the poppy (papaver somniferum). Crystallized morphin ($\dot{M}o + H_2 O$) usually appears in the form of colorless, brilliant rhombic prisms, or, when obtained by precipitation, as a white crystalline powder. It has a bitter taste, and dissolves very sparingly in cold, but somewhat more readily in boiling water. Of cold alcohol it requires about 90 parts by weight for solution; of boiling alcohol from 20 to 30 parts. The solutions of morphin in alcohol, as well as in hot water, manifest distinctly alkaline reaction. Morphin is nearly insoluble in ether, especially when crystallized, it dissolves in hot amylic alcohol, it is insoluble in benzol (RODGERS), and very difficultly soluble in chloroform (PETTENKOFER). Crystallized morphin loses its water at a moderate heat. Morphin may be sublimed unaltered by very cautious heating.*

2. Morphin neutralizes acids completely, and forms with them the MORPHIN SALTS. These salts are readily soluble in water and alcohol, insoluble in ether and amylic alcohol; their taste is disagreeably bitter. Most of them are crystallizable.

3. *Potassa and ammonia* precipitate from the solutions of morphin salts—generally only after some time—$\dot{M}o + H_2 O$, in the form of a white crystalline powder. Stirring and fric-

* For the best way of subliming morphin, and for the value of the sublimate in microscopic diagnosis, see HELWIG (Zeitschr. f. anal. Chem., 3, 43; or Das Mikroscop in der Toxikologie, von Dr. A. HELWIG. Von Zabern, Mainz, 1864). In the latter work the subject is treated more completely, and illustrated. I may mention that the alkaloid must be perfectly pure.

tion on the sides of the vessel promote the separation of the precipitate, which redissolves with great readiness in an excess of potassa, but more sparingly in ammonia. It dissolves also in ammonium chloride, and, though with difficulty only, in ammonium carbonate. On shaking a solution of morphin in potassa or soda with ether, very little of the alkaloid passes into the ether; on shaking with warm amylic alcohol, however, the whole of the alkaloid passes into the latter.

4. *Potassium carbonate and sodium carbonate* produce the same precipitate as potassa and ammonia, but fail to redissolve it upon addition in excess. Consequently if a fixed alkali bicarbonate is added to a solution of morphin in caustic potassa, or if carbon dioxide is conducted into the solution, $\dot{M}o + H_2O$ separates, especially after ebullition, in the form of a crystalline powder. A more minute inspection, particularly through a lens, shows this powder to consist of small acicular crystals; magnified 100 times, these crystals present the form of rhombic prisms.

5. *Sodium bicarbonate and potassium bicarbonate* speedily produce in neutral solutions of morphin salts a precipitate of morphin hydrate in the form of a crystalline powder. The precipitate is insoluble in an excess of the precipitants. These reagents fail to precipitate acidified solutions of morphin salts in the cold.

6. The action of strong *nitric acid* upon morphin or one of its salts, in the solid state or in concentrated solutions, produces a yellowish-red color. On addition of stannous chloride no violet coloration occurs, as in the case of brucin. Dilute solutions do not change their color upon addition of nitric acid in the cold, but upon heating they acquire a yellow tint.

7. If morphin or a morphin compound is treated with 4 or 5 drops of pure, strong *sulphuric acid*, and warmed on a water bath for 15 minutes, a colorless solution is obtained; if, after cooling, 10 to 20 drops of *sulphuric acid, mixed with nitric acid*,* are added, and 2 or 3 drops of water, the fluid acquires a violet-red color (gentle heating promotes the reaction); and if now 4 or 5 clean lentil-sized fragments of

* Mix 6 drops of nitric acid of 1.33 sp. gr. with 100 c.c. water, and add 10 drops of this mixture to 20 grammes of pure concentrated sulphuric acid.

manganese dioxide are added, or a fragment of *potassium chromate* (OTTO), the fluid acquires an intense mahogany color. If the fluid is then diluted with 4 parts of water, cooled in a test tube, and ammonia added till the reaction is almost neutral, a dirty yellow color makes its appearance, which turns brownish red upon supersaturation with ammonia, without the deposition of any appreciable precipitate (J. ERDMANN). According to A. HUSEMANN* the violet coloration of morphin sulphate by nitric acid does not occur till the morphin solution has undergone change. It occurs immediately when the solution in strong sulphuric acid is heated to 100°–150°. If, after cooling, a drop of nitric acid is added, a splendid dark violet color is produced, which stays at the edge for several minutes, but in the middle soon passes into a blood-red color, which slowly becomes paler. Sodium hypochlorite acts like nitric acid. On heating morphin with sulphuric acid above 150°, a transient reddish-violet color is produced, which turns finally to dirty green. If a solution which has thus been overheated is brought in contact after cooling with nitric acid, no bluish-violet color is observed, but a reddish color is at once produced.

8. If a solution of *molybdic acid in concentrated sulphuric acid* (5 mgrm. sodium molybdate and 1 c.c. conc. sulphuric acid) is mixed with dry morphin or a dry morphin salt, a magnificent reddish-violet color will make its appearance immediately; after a time the color will turn a dirty greenish brown. The experiment should be made in a small porcelain dish or watch glass, and the mixture should be stirred with a glass rod. On further action of the air the fluid will become deep blue, commencing at the edge; this color will remain for hours (FRÖHDE).† If water is added to the blue fluid, this color vanishes, and a slightly turbid, dirty brown fluid is obtained; when this is filtered it yields a brown filtrate. (Difference from salicin.)

9. *Ferric chloride* imparts to *concentrated* neutral solutions of morphin salts a beautiful dark blue color, which disappears upon the addition of an acid. If the solution contains an admixture of animal or vegetable extractive matters, or of acetates, the color will appear less distinctly.

* Zeitschr. f. anal. Chem., 8, 151.

† Zeitschr. f. anal. Chem., 5, 214.

10. If *iodic acid* is added to a solution of morphin or of a morphin salt, IODINE separates. In concentrated aqueous solutions the separated iodine appears as a kermes-brown precipitate, whilst to alcoholic and dilute aqueous solutions it imparts a brown or yellowish-brown color. The addition of starch paste to the fluid, before or after that of the iodic acid, considerably heightens the delicacy of the reaction, since the blue tint of the iodized starch remains perceptible in exceedingly dilute solutions, which is not the case with the brown color imparted by iodine. The reaction is most delicate when the iodic acid solution is mixed with starch paste, and the dry morphin salt is added to the mixture. It needs scarcely be mentioned that the delicacy of the reaction may also be increased by shaking with carbon disulphide. As other nitrogenous bodies (albumin, casein, fibrin, etc.) likewise reduce iodic acid, this reaction has only a relative value; however, if *ammonia* is added after the iodic acid, the fluid becomes colorless if the separation of iodine has been caused by other substances, whilst the coloration becomes much more intense if it is owing to the presence of morphin (LEFORT).*

11. *Tannic acid* throws down in aqueous solutions of morphin salts, if they are not too dilute, white precipitates, readily soluble in acids.

SECOND GROUP.

NON-VOLATILE ALKALOIDS WHICH ARE PRECIPITATED BY POTASSA FROM THE SOLUTIONS OF THEIR SALTS, BUT DO NOT REDISSOLVE TO A PERCEPTIBLE EXTENT IN AN EXCESS OF THE PRECIPITANT, AND ARE PRECIPITATED BY SODIUM BICARBONATE EVEN FROM ACID SOLUTIONS, if the latter are not diluted in a larger proportion than 1 : 100; Narcotin, Quinin, Cinchonin.

a. NARCOTIN ($C_{22}H_{23}NO_7 = \overset{+}{N}a$).

§ 227.

1. Narcotin accompanies morphin in opium (§ 226). Crys-

* LEFORT (Zeitschr. f. anal. Chem., 1, 134) recommends the following method for the detection of small quantities of morphin: moisten strips of very white unsized paper with the morphin solution, dry, and repeat the operation several times, so as to insure absorption by the paper of a tolerably large quantity of the fluid; the dried paper contains the morphin in the solid state, most finely divided. Nitric acid, ferric chloride, and iodic acid and ammonia will readily and with positive distinctness show the characteristic reactions on paper so prepared.

tallized narcotin appears usually in the form of colorless, brilliant, right rhombic prisms, or, when precipitated by alkalies, as a white, loose, crystalline powder. It is insoluble in water. Alcohol and ether dissolve it sparingly in the cold, but somewhat more readily upon heating. Chloroform dissolves it very easily, amylic alcohol with difficulty, benzol more readily. Solid narcotin is tasteless, but the alcoholic and ethereal solutions are intensely bitter. Narcotin does not alter vegetable colors.

2. Narcotin dissolves readily in acids, combining with them to form salts. These salts have invariably an acid reaction. Those with weak acids are decomposed by a large amount of water, and if the acid is volatile, even upon simple evaporation. Most of the salts of narcotin are amorphous, and soluble in water, alcohol, and ether; they have a bitter taste.

3. *Pure alkalies* and *alkali carbonates* and *bicarbonates* immediately precipitate narcotin from the solutions of its salts, in the form of a white powder, which, magnified 100 times, appears an aggregate of small crystalline needles. The precipitate is insoluble in an excess of the precipitants. If solution of a narcotin salt is mixed with ammonia, and ether added in sufficient quantity, the precipitate redissolves in the ether, and the clear fluid presents two distinct layers. If a drop of the ethereal solution is evaporated on a watch glass, the residue is seen, when magnified 100 times, to consist of small, distinct, elongated, and lance-shaped crystals.

4. *Concentrated nitric acid* dissolves narcotin to a colorless fluid, which acquires a pure yellow tint upon application of heat.

5. *Strong sulphuric acid* acts differently upon different specimens of narcotin. Those that are apparently the purest give a bluish-violet solution which in a short time becomes dirty orange; specimens which appear less pure give a yellow solution at once. If the yellow solution in either case is warmed *very gradually* it becomes at first orange-red, subsequently beautiful bluish-violet, or purple-blue stripes are seen proceeding from the edge, and finally, when the sulphuric acid begins to evaporate, an intense reddish-violet color is formed. If the heating is interrupted when the blue color is present, the solution slowly becomes cherry-red in the cold. The reaction is very delicate (HUSEMANN.) *

* Zeitschr. f. anal. Chem., 3, 151.

6. If to a solution of narcotin in strong sulphuric acid prepared in the cold, 10 to 20 drops of sulphuric acid containing a minute quantity of *nitric acid* (foot-note, p. 448) are added, and then two or three drops of water, the fluid becomes intensely red. Slight warming is favorable to the reaction. Addition of manganese dioxide does not change the color. If, after dilution, ammonia is added till the fluid is *nearly* neutral, the intensity of the color is diminished in consequence of the dilution. On addition of excess of ammonia, a copious dark-brown precipitate is finally produced (J. ERDMANN).

If to a solution of narcotin in strong sulphuric acid, prepared in the cold, sodium hypochlorite is added, a distinct and rather permanent crimson color is produced, which passes into yellowish-red. The solution of narcotin in strong sulphuric acid, which has been colored by heat, is turned immediately light yellow by nitric acid or sodium hypochlorite, and a more reddish coloration appears gradually (HUSEMANN).

7. *Chlorine water* added to solution of narcotin salt gives a yellow color, slightly inclining to green. On the addition of ammonia a yellowish-red and much more intense color is produced.

8. If narcotin or a salt of narcotin is dissolved in excess of dilute *sulphuric acid*, mixed with finely powdered *manganese dioxide*, and boiled for some minutes, the alkaloid is converted into opianic acid, cotarnin (a base soluble in water), and carbon dioxide. On filtering, and adding ammonia to the filtrate, no precipitate will be obtained.

9. *Tannic acid* produces whitish precipitates in solution of salts of narcotin. When the solutions are very dilute a mere turbidity is produced, but a precipitate is formed on addition of a drop of hydrochloric acid. The precipitate is very slightly soluble in hydrochloric acid.

b. QUININ ($C_{20}H_{24}N_2O_2 = \dot{Q}$).

§ 228.

1. Quinin occurs in cinchona bark accompanying cinchonin. Crystallized quinin ($\dot{Q} + 3H_2O$), appears either in the form

of fine crystalline needles of silky lustre, which are frequently aggregated into tufts, or as a loose white powder. It is sparingly soluble in cold, but somewhat more readily in hot water. It is readily soluble in alcohol, both cold and hot, but less so in ether. The taste of quinin is intensely bitter; the solutions of quinin manifest alkaline reaction. Upon exposure to heat it loses 3 H_2O.

2. Quinin neutralizes acids completely. The neutral salts taste intensely bitter; most of them are crystallizable, difficultly soluble in cold, readily soluble in hot water, and in alcohol. The acid salts dissolve very freely in water; the solutions reflect a bluish tint. If a cone of light is thrown into them, by means of a lens, either horizontally or vertically, a blue cone of light is seen even in highly dilute solutions.

3. *Potassa*, *ammonia*, and the normal *alkali carbonates* produce in solutions of quinin salts (if they are not too dilute) a white, loose, pulverulent precipitate of hydrated quinin, which immediately after precipitation appears opaque and amorphous under the microscope, but assumes, after the lapse of some time, the appearance of an aggregate of crystalline needles. The precipitate redissolves only to a scarcely perceptible extent in an excess of potassa, but more so in ammonia. It is hardly more soluble in fixed alkali carbonates than in pure water. Ammonium chloride increases its solubility in water. If a solution of quinin is mixed with ammonia, ether added, and the mixture shaken, the quinin redissolves in the ether, and the clear fluid presents two distinct layers. (In this point quinin differs essentially from cinchonin, which by this means may be readily detected in presence of the former, and separated from it.)

4. *Sodium bicarbonate* also produces, both in neutral and acid solutions of quinin salts, a white precipitate. In acidified solutions containing 1 part of quinin to 100 parts of acid and water, the precipitate forms immediately; if the proportion of the quinin to the acid and water is 1 : 150, the precipitate separates only after an hour or two, in the form of distinct needles, aggregated into groups. If the proportion is 1 : 200, the fluid remains clear, and it is only after from twelve to twenty-four hours' standing that a slight precipitate makes its appearance. The precipitate is not altogether insoluble in the precipitant, and the separation is accordingly the more

complete the less the excess of the precipitant; the precipitate contains carbonic acid.

5. *Concentrated nitric acid* dissolves quinin to a colorless fluid, turning yellowish upon application of heat.

6. The addition of *chlorine water* to the solution of a salt of quinin fails to impart a color to the fluid, or, at least, imparts to it only a very faint tint; but if ammonia is now added, the fluid acquires an intense emerald-green color. If, after the addition of the chlorine water, some solution of *potassium ferrocyanide* is added, then a few drops of *ammonia* or some other alkali, the fluid acquires a magnificent deep-red tint, which, however, speedily changes to a dirty brown. This reaction is delicate and characteristic. Upon addition of an acid * to the red fluid, the color vanishes, but reappears afterwards upon cautious addition of ammonia. (O. LIVONIUS, communicated; A. VOGEL.)

7. *Concentrated sulphuric acid* dissolves pure quinin and pure quinin salts to a colorless or very faint yellowish fluid; application of a gentle heat turns the fluid yellow, application of a stronger heat brown. Sulphuric acid containing an admixture of nitric acid dissolves quinin to a colorless or very faint yellowish fluid.

8. *Tannic acid* produces a white precipitate in aqueous solutions of quinin salts, even when they are exceedingly dilute. The precipitate is curdy, and agglutinates on warming; it is soluble in acetic acid.

9. As regards HERAPATH'S quinin reaction, based upon the polarizing properties of quinin iodo-sulphate, I refer to *Phil. Mag.*, 6, 171.

c. CINCHONIN ($C_{20}H_{24}NO_2 = \dot{C}i$).

§ 229.

1. Cinchonin occurs in cinchona bark, accompanying quinin. It appears either in the form of transparent, brilliant, rhombic prisms, or fine white needles, or, if precipitated from concentrated solutions, as a loose white powder. At first it is tasteless, but after some time a bitter taste of bark becomes perceptible. It is nearly insoluble in cold water, and dis-

* Acetic acid answers the purpose best.

solves only with extreme difficulty in hot water; it dissolves sparingly in cold dilute alcohol, more readily in hot alcohol, and the most freely in absolute alcohol. From hot alcoholic solutions the greater portion of the dissolved cinchonin separates upon cooling in a crystalline form. Solutions of cinchonin taste bitter, and manifest alkaline reaction. Cinchonin is insoluble in ether.*

2. Cinchonin neutralizes acids completely. The salts have the bitter taste of bark; most of them are crystallizable; they are generally more readily soluble in water and in alcohol than the corresponding quinin compounds. Ether fails to dissolve them.

3. Cinchonin, when heated cautiously, fuses at first without loss of water; subsequently white fumes arise which, like benzoic acid, condense upon cold substances, in the form of small brilliant needles, or as a loose sublimate, a peculiar aromatic odor being exhaled at the same time. If the operation is conducted in a stream of hydrogen gas, long brilliant prisms are obtained (HLASIWETZ).

4. *Potassa, ammonia* and the *normal alkali carbonates* produce in solutions of cinchonin salts a white loose precipitate of CINCHONIN, which does not redissolve in an excess of the precipitants. If the solution was concentrated, the precipitate does not exhibit a distinctly crystalline appearance, even when magnified 200 times; but if the solution was so dilute that the precipitate formed only after some time, it appears under the microscope to consist of distinct crystalline needles aggregated into star-shaped tufts.

5. *Sodium bicarbonate* and *potassium bicarbonate* precipitate cinchonin in the same form as in 4, both from neutral and acidified solutions of cinchonin salts, but not so completely as the alkali monocarbonates. Even in solutions containing 1 part of cinchonin to 200 of water and acid, the precipitate forms immediately; its quantity, however, increases after standing some time.

6. *Concentrated sulphuric acid* dissolves cinchonin to a colorless fluid, which upon application of heat first acquires a brown, and finally a black color. Addition of some nitric

* The cinchonin of commerce usually contains in admixture another alkaloid, called cinchotin, which is soluble in ether. This alkaloid crystallizes in large rhomboidal crystals of brilliant lustre, which fuse at a high temperature, and cannot be sublimed, even in a stream of hydrogen gas (HLASIWETZ).

acid leaves the solution colorless in the cold, but upon application of heat the fluid, after passing through the intermediate tints of yellowish-brown and brown, turns finally black.

7. The addition of *chlorine water* to the solution of a cinchonin salt fails to impart a color to the fluid; if ammonia is now added, a yellowish-white precipitate is formed.

8. If the solution of a cinchonin salt, containing only very little or no free acid, is mixed with *potassium ferrocyanide*, a flocculent precipitate of cinchonin ferrocyanide is formed. If an excess of the precipitant is added, and a gentle heat very slowly applied, the precipitate dissolves, but separates again upon cooling, in brilliant gold-yellow scales, or in long needles, often aggregated in the shape of a fan. With the aid of the microscope, this reaction is as delicate as it is characteristic (CH. DOLLFUS, BILL, SELIGSOHN).

9. *Tannic acid* produces a white flocculent precipitate in aqueous solutions of cinchonin salts; the precipitate is soluble in a small quantity of hydrochloric acid, but is reprecipitated by addition of more hydrochloric acid.

Recapitulation and Remarks.

§ 230.

Narcotin and quinin, being soluble in ether, whilst cinchonin is insoluble, the two former alkaloids may be most readily separated by this means from the latter. For this purpose the analyst need simply mix the aqueous solution of the salts with ammonia in excess, then add ether, and separate the solution of quinin and narcotin from the undissolved cinchonin. If the ethereal solution is now evaporated, the residue dissolved in hydrochloric acid, and a sufficient amount of water to make the dilution 1 : 200, and sodium bicarbonate is then added, the narcotin precipitates, whilst the quinin remains in solution. By evaporating the solution, and treating the residue with water, the quinin is obtained in the free state.*

* The reaction with ammonia and ether fails to effect the separation of quinin from various other bases found associated with it, viz.: α quinidin, β quinidin, γ quinidin, and cinchonidin; since, as G. KERNER (Zeitschr. f. anal. Chem., 1, 150) has shown, several of these other alkaloids are pretty freely soluble in ether. In fact, no qualitative reaction will enable the analyst to fully effect this purpose; but it may be accomplished by means of a simple volu-

THIRD GROUP.

NON-VOLATILE ALKALOIDS WHICH ARE PRECIPITATED BY POTASSA FROM THE SOLUTIONS OF THEIR SALTS, AND DO NOT REDISSOLVE TO A PERCEPTIBLE EXTENT IN AN EXCESS OF THE PRECIPITANT;* BUT ARE NOT PRECIPITATED FROM (even somewhat concentrated) ACID SOLUTIONS BY THE BICARBONATES OF THE FIXED ALKALI METALS: Strychnin, Brucin, Veratrin, Atropin.

a. STRYCHNIN ($C_{21}H_{22}N_2O_2 = \overset{+}{S}r$).

§ 231.

1. Strychnin exists in company with brucin in various kinds of strychnos, especially in the fruit of strychnos nux vomica and of strychnos ignatius. It appears either in the form of white, brilliant, rhombic prisms, or when produced by precipitation or rapid evaporation, as a white powder. It has an exceedingly bitter taste. It is nearly insoluble in cold, and barely soluble in hot water. It is almost insoluble in absolute alcohol and ether, and only sparingly soluble in dilute alcohol. It dissolves freely in amylic alcohol, more especially with the aid of heat, likewise in benzol (RODGERS) and chloroform (PETTENKOFER). It does not fuse when heated. By cautious heating it may be sublimed unaltered (HELWIG), see foot-note § 226, 1.

2. Strychnin neutralizes acids completely. The strychnin salts are, for the most part, crystallizable; they are soluble in water, have an intolerably bitter taste, and are, like the pure alkaloid, exceedingly poisonous.

3. *Potassa* and *sodium carbonate* produce in solutions of strychnin salts white precipitates of STRYCHNIN, which are insoluble in an excess of the precipitants. Magnified 100 times the precipitate appears as an aggregate of small crystalline needles. From dilute solutions the strychnin separates only after the lapse of some time, in the form of crystalline needles, distinctly visible to the naked eye.

metrical method, based upon the circumstance that the quinin thrown down by ammonia from a solution of the sulphate, requires less ammonia to redissolve it than all the other alkaloids of the bark. Concerning the separation of quinin from quinidin, compare SCHWARZER (Zeitschr. f. anal. Chem., 4, 120), and concerning the separation of the cinchona alkaloids in general, see VAN DER BURG (Zeitschr. f. anal. Chem., 4, 273).

* Regarding atropin, see § 241, 4.

4. *Ammonia* produces the same precipitate as potassa. The precipitate redissolves in an excess of ammonia; but after a short time—or if the solution is highly dilute, after a more considerable time—the strychnin crystallizes from the ammoniacal solution in the form of needles, which are distinctly visible to the naked eye.

5. *Sodium bicarbonate* produces in neutral solutions of strychnin salts a precipitate of strychnin, which separates in fine needles shortly after the addition of the reagent, and is insoluble in an excess of the precipitant. But upon adding one drop of acid (so as to leave the fluid still alkaline), the precipitate dissolves readily in the liberated carbonic acid. The addition of sodium bicarbonate to an acid solution of strychnin causes no precipitation, and it is only after the lapse of twenty-four hours, or even a longer period, that strychnin crystallizes from the fluid in distinct prisms, in proportion as the free carbonic acid escapes. If a concentrated solution of strychnin, supersaturated with sodium bicarbonate, is boiled for some time, a precipitate forms at once; from dilute solutions this precipitate separates only after concentration.

6. *Potassium sulphocyanate* produces in concentrated solutions of strychnin salts immediately, in dilute solutions after the lapse of some time, a white crystalline precipitate, which appears under the microscope as an aggregate of flat needles, truncated or pointed at an acute angle, and is but little soluble in an excess of the precipitant.

7. *Mercuric chloride* produces in solutions of strychnin salts a white precipitate, which changes after some time to crystalline needles, aggregated into stars, and distinctly visible through a lens. Upon heating the fluid these crystals redissolve, and upon subsequent cooling of the solution the compound recrystallizes in larger needles.

8. If a few drops of pure *concentrated sulphuric acid* are added to a little strychnin in a porcelain dish, solution ensues, without coloration of the fluid. If small quantities of oxidizing agents (potassium chromate, permanganate, or ferricyanide, lead dioxide, or manganese dioxide) are now added—best in the solid form, as dilution is prejudicial to the reaction—the fluid acquires a magnificent blue-violet color, which, after some time, changes to wine-red, then to reddish-yellow. With potassium chromate or permanganate the reaction is

immediate; on inclining the dish, blue-violet streaks are seen to flow from the salt fragment, and by pushing the latter about, the coloration is soon imparted to the entire fluid. With potassium ferricyanide the reaction is less rapid; but it is slowest with dioxides. The more speedy the manifestation of the reaction, the more rapid is also the change of color from one tint to another. I prefer potassium chromate, recommended by OTTO, or potassium permanganate, recommended by GUY, to all other oxidizing agents. JORDAN succeeded, with chromate, in distinctly showing the presence of $\frac{1}{50000}$ grain of strychnin. J. ERDMANN prefers manganese dioxide in lentil-sized fragments. Metallic chlorides and considerable quantities of nitrates, also large quantities of organic substances, prevent the manifestation of the reaction, or impair its delicacy. It is therefore always advisable to free the strychnin first, as far as practicable, from all foreign matters before proceeding to try this reaction. If the solution colored red (by manganese dioxide) is mixed with from 4 to 6 times its volume of water, heating being avoided, and ammonia is then added until the reaction is *nearly* neutral, the fluid shows a magnificent violet-purple tint; upon addition of more ammonia the color becomes yellow-green to yellow (J. ERDMANN). I have found, however, that this reaction is seen only where larger, though still very minute, quantities of strychnin are present. Morphin interferes with this reaction.* In order to remove the morphin, the concentrated aqueous neutral solution of the substance is mixed with potassium ferricyanide (NEUBAUER) or normal potassium chromate (HORSLEY) and filtered. The precipitate contains the strychnin, the solution the morphin. The precipitate is washed a little, dried, and mixed in a watch glass with strong sulphuric acid. The blue-violet color is immediately produced. It should be borne in mind that the strychnin precipitates are not insoluble in water.† Finally, I must mention that curarin produces the same reaction with sulphuric acid and potassium chromate as strychnin. They differ, however, in this, that curarin is colored red by sulphuric acid alone, and it gives

* REESE, Zeitschr. f. anal. Chem., 1, 399. HORSLEY, *ibid.*, 1, 515. THOMAS, *ibid.*, 1, 517.

† RODGERS recommends to separate strychnin from morphin by benzol, in which the former alone is soluble. THOMAS recommends to render the solution of the acetates alkaline with potash, and to shake with chloroform; the morphin remains in the alkaline solution, while the strychnin dissolves in the chloroform.

much more permanent colorations with the chromate than strychnin (DRAGENDORFF).

9. Strong *chlorine water* produces in solutions of strychnin salts a white precipitate, soluble in ammonia to a colorless fluid.

10. Strong *nitric acid* dissolves strychnin and its salts to a colorless fluid, which turns yellow when heated.

11. *Tannic acid* produces in solutions of strychnin salts heavy white precipitates, insoluble in hydrochloric acid.

b. BRUCIN ($C_{23}H_{26}N_2O_4 = \overset{+}{B}r$).

§ 232.

1. Brucin occurs with strychnin (see § 231). Crystallized brucin ($\overset{+}{B}r + 4H_2O$) appears either in the form of transparent straight rhombic prisms, or in that of crystalline needles aggregated into stars, or as a white powder composed of minute crystalline scales. Brucin is difficultly soluble in cold, but somewhat more readily in hot water. It dissolves freely in alcohol, both in absolute and dilute, also in cold, but more readily still in hot amylic alcohol; but it is almost insoluble in ether. Its taste is intensely bitter. When heated it fuses with loss of its crystal water. By cautious heating it may be sublimed unchanged (see foot-note, § 226, 1).

2. Brucin neutralizes acids completely. The salts of brucin are readily soluble in water, and of an intensely bitter taste. Most of them are crystallizable.

3. *Potassa* and *sodium carbonate* throw down from solutions of brucin salts a white precipitate of brucin, insoluble in an excess of the precipitant. Viewed under the microscope, immediately after precipitation, it appears to consist of very minute grains; but upon further inspection, these grains are seen—with absorption of water—to suddenly form into needles, which latter subsequently arrange themselves without exception into concentric groups. These successive changes of the precipitate may be traced distinctly even with the naked eye.

4. *Ammonia* produces in solutions of brucin salts a whitish precipitate, which appears at first like a number of minute drops of oil, but changes subsequently—with absorption of water—to small needles. The precipitate redissolves, imme-

diately after separation, very readily in an excess of the p cipitant; but after a very short time—or, in dilute solutio after a more considerable lapse of time—the brucin, combi with crystal water, crystallizes from the ammoniacal fluid small concentrically grouped needles, which addition of a monia fails to redissolve.

5. *Sodium bicarbonate* produces in neutral solutions of b cin salts a precipitate of brucin, combined with crystal wat this precipitate separates, after the lapse of a short time, form of concentrically aggregated needles of silky lust which are insoluble in an excess of the precipitant, but d solve in free carbonic acid (compare *Strychnin*). Sodium carbonate fails to precipitate acid solutions of brucin sal and it is only after the lapse of a considerable time, and w the escape of the carbonic acid, that the alkaloid separa from the fluid in regular and comparatively large crystals.

6. *Concentrated nitric acid* dissolves brucin and its salts intensely red fluids, which subsequently acquire a yellowi red tint, and turn yellow upon application of heat. Up addition of stannous chloride or ammonium sulphide to t heated fluid, no matter whether concentrated or after diluti with water, the faint yellow color changes to a most inter violet.

7. If a little brucin is treated with from 4 to 6 drops pure *concentrated sulphuric acid*, a solution of a faint rose col is obtained, which afterwards turns yellow. If 10 or 20 dro of sulphuric acid mixed with some *nitric acid* (foot-note, § 2 7) are added, the fluid transiently acquires a red, afterwar a yellow color. Addition of manganese dioxide transient imparts a red, then a gamboge tint to the fluid. If the flu is then, with proper cooling, diluted with 4 parts of wat and *ammonia* added to nearly neutral reaction, or even alkaline reaction, the solution acquires a gold-yellow col ERDMANN).

8. Addition of *chlorine water* to the solution of a salt brucin imparts to the fluid a fine bright-red tint; if ammon is then added, the red color changes to yellowish brown.

9. *Potassium sulphocyanate* produces in concentrated sol tions of salts of brucin immediately, in dilute solutions aft some time, a granular crystalline precipitate, which, under t microscope, appears composed of variously aggregated pol

hedral crystalline grains. Friction applied to the sides of the vessel promotes the separation of the precipitate.

10. *Mercuric chloride* also produces a white granular precipitate, which, under the microscope, appears composed of small roundish crystalline grains.

11. *Tannic acid* produces in solutions of salts of brucin heavy dirty white precipitates, soluble in acetic acid, insoluble in hydrochloric acid.

c. VERATRIN ($C_{32}H_{52}N_2O_8$) $\overset{+}{Ve}$.

§ 233.

1. Veratrin occurs in various species of veratrum, especially in the seeds of veratrum sabadilla (with veratric acid), and in the root of veratrum album (with jervin). It appears in the form of small prismatic crystals, which acquire a porcelain-like look in the air, or as a white powder of acrid and burning, but not bitter taste; it is exceedingly poisonous. Veratrin acts with great energy upon the membranes of the nose; even the most minute quantity of the powder excites the most violent sneezing. It is insoluble in water; in alcohol it dissolves readily, but more sparingly in ether. At 115° it fuses like wax, and solidifies upon cooling to a transparent yellow mass. By cautious heating it may be sublimed unchanged (see foot-note, § 226, 1).

2. Veratrin neutralizes acids completely. Some veratrin salts are crystallizable, others dry up to a gummy mass. They are soluble in water, and have an acrid and burning taste.

3. *Potassa, ammonia* and the *alkali monocarbonates* produce in solutions of veratrin salts a flocculent white precipitate, which, viewed under the microscope immediately after precipitation, does not appear crystalline. After the lapse of a few minutes, however, it alters its appearance, and small scattered clusters of short prismatic crystals are observed, instead of the original coagulated flakes. The precipitate does not redissolve in an excess of potassa or of potassium carbonate. It is slightly soluble in ammonia in the cold, but the dissolved portion separates again upon application of heat.

4. With *sodium bicarbonate* and *potassium bicarbonate* the salts of veratrin comport themselves like those of strychnin and

brucin. However, the veratrin separates readily upon boiling, even from dilute solutions.

5. If veratrin is acted upon by *concentrated nitric acid*, it agglutinates into small resinous lumps, which afterwards dissolve slowly in the acid. If the veratrin is pure the solution is colorless.

6. If veratrin is treated with *concentrated sulphuric acid*, it also agglutinates at first into small resinous lumps; but these dissolve with great readiness to a faint yellow fluid, the color of which gradually increases in depth and intensity, and changes afterwards to a reddish-yellow, then to an intense blood-red, and finally to purple-red. The color persists 2 or 3 hours, then disappears gradually. Addition of sulphuric acid, containing nitric acid, or of manganese dioxide, causes no great change of color. If the fluid is then diluted with water, and ammonia added until the reaction is nearly neutral, a yellowish solution is obtained, in which ammonia added in excess produces a greenish light-brown precipitate (J. ERDMANN).

7. If veratrin is dissolved in *strong hydrochloric acid*, a colorless fluid is obtained, which by long boiling acquires an intensely red tint, permanent on standing. The reaction is very delicate, and occurs not only with the perfectly pure veratrin, but with the ordinary commercial alkaloid (TRAPP).

8. *Potassium sulphocyanate* produces only in concentrated solutions of veratrin salts flocculent gelatinous precipitates.

9. Addition of *chlorine water* to the solution of a veratrin salt imparts to the fluid a yellowish tint, which upon addition of ammonia, changes to a faint brownish color. In concentrated solutions chlorine produces a white precipitate.

d. ATROPIN ($C_{17}H_{23}NO_3$).

§ 234.

1. Atropin occurs in all parts of the deadly nightshade (atropa belladonna) and of the thorn-apple (datura stramonium). It forms small brillant prisms and needles. It is, when pure, without odor and nauseously bitter; it fuses at 90°, and volatilizes at 140° with partial decomposition. By

heating between watch glasses it volatilizes without blackening. The sublimate is soft and oily. Atropin dissolves in about 300 parts of cold water, and 60 parts of boiling water; it is very soluble in alcohol, the saturated alcoholic solution is precipitated by addition of a small quantity of water. It is very soluble in chloroform and amylic alcohol, but it requires about forty parts of ether for solution.

2. Atropin combines with acids, forming salts, some of which, particularly the acid salts, do not crystallize. The salts dissolve easily in water and alcohol, scarcely at all in ether. The aqueous solutions of the salts acquire a dark color by long heating.

3. Atropin and its salts are active narcotic poisons. When applied to the eye they dilate the pupil for a considerable time. Hyoscyamin has the same action; but the dilatation in this case is rather slower in making its appearance, and more lasting.

4. *Potassa* and *fixed alkali monocarbonates*, added to concentrated aqueous solutions of atropin salts, precipitate a portion of the alkaloid. The precipitate, which is at first pulverulent, does not dissolve in excess of the precipitant more readily than in water. By long standing it becomes crystalline. *Ammonia* likewise produces a precipitate, soluble in excess. Atropin is decomposed in contact with fixed alkalies or with baryta water, slowly in the cold, rapidly on heating.

5. *Ammonium carbonate* and *alkali bicarbonates* do not precipitate solutions of salts of atropin.

6. *Hydrochlorauric acid*, added to aqueous solutions of atropin salts, throws down atropin hydrochlorauride in the form of a yellow precipitate, which gradually turns crystalline.

7. *Tannic acid* produces in aqueous solutions of salts of atropin a white curdy precipitate soluble in ammonia.

8. If atropin is warmed with concentrated *sulphuric acid* to slight browning, and a few drops of water are added, an agreeable odor is evolved, recalling the sloe blossom, or perhaps more the galium verum. On further heating the odor increases.

9. *Cyanogen gas*, passed into a sufficiently concentrated alcoholic solution of atropin, produces a reddish-brown color (HINTERBERGER).

10. *Picric acid* does not precipitate solutions of pure salts

C. Properties and Reactions of certain non-nitrogenous Bodies allied to the Alkaloids, viz., Salicin, Digitalin and Picrotoxin.

§ 236.

a. Salicin ($C_{13}H_{18}O_7$).

1. Salicin exists in the bark and leaves of most kinds of willow and some kinds of poplar. It appears either in the form of white crystalline needles and scales of silky lustre, or, where the crystals are very small, as a powder of silky lustre. It has a bitter taste, is readily soluble in water and alcohol, but insoluble in ether.

2. No reagent precipitates salicin as such.

3. If salicin is treated with *concentrated sulphuric acid*, it agglutinates into a resinous lump, and acquires an intensely blood-red color, without dissolving; the color of the sulphuric acid is at first unaltered.

4. If an aqueous solution of salicin is mixed with *hydrochloric acid* and boiled for a short time, it suddenly becomes turbid with formation of sugar, and deposits a white agglutinating precipitate (saliretin). If the precipitated liquor is now mixed with 1 or 2 drops of potassium chromate and boiled, the saliretin will acquire a bright rose color, the characteristic odor of salicyl-aldehyd being emitted at the same time.

§ 237.

b. Digitalin ($C_{25}H_{40}O_{15}$?).

1. Digitalin exists in the leaves, seeds, and capsules of the fox-glove (digitalis purpurea). It is usually white, amorphous, but it may also be obtained in crystals.* It is without odor, bitter, and an active poison; its powder irritates the eyes and causes sneezing. At 180° it becomes colored, but does not fuse, above 200° it is completely decomposed.

2. Digitalin is neutral. It dissolves in all proportions in chloroform, and in about 12 parts of alcohol of 90° at the ordinary temperature, but more readily on boiling; it is less

* Nativelle gives a method for preparing crystallized digitalin (see Journ. de Pharm., 9, 265—Zeitschr. f. Chem. 5, 401—Chem. Centr. Bl., 1870, 30). The commercial digitalin is frequently a mixture of various bodies, and this explains why the properties of digitalin, as given by different chemists, are found to vary so greatly.

soluble in absolute alcohol. It is only very slightly in ether free from alcohol. It is very difficultly so water, even when boiling (1 part requires 1,000 parts ing water), the solution, however, has a very bitter ta

3. When digitalin is dissolved in *concentrated sulph* (to which it imparts a green color), and the solution i with a rod dipped in *bromine water*, a violet-reddish tion makes its appearance (GRANDEAU, J. OTTO). W experiment is made in the manner directed the rea very delicate and characteristic. Delphinin only s similar deportment; but when an acid solution is shak ether, delphinin does not pass into the ether, while d does (OTTO).

4. *Hydrochloric acid* dissolves digitalin with a gr yellow color; water precipitates a resinous body fr solution. *Nitric acid* dissolves it with evolution of red *Acetic acid* dissolves it without being colored.

5. On shaking a solution of digitalin, even if aci *ether*, the digitalin passes into the ether (J. OTTO).

6. The solutions of digitalin are not precipitated by *of iodine, picric acid*, and *metallic salts*, but they are p tated by *tannic acid*. The precipitate is somewhat sol boiling water.

7. On boiling digitalin with *dilute sulphuric acid*, sug digitaliretin are formed (WALZ, KOSSMANN). The form be recognized by its power of reducing alkaline solu copper, the latter crystallizes from hot alcohol in bi grains (KOSSMANN). J. OTTO says that on boiling d solution of digitalin in dilute sulphuric acid an odor re infusion of digitalis is noticed.

§ 238.

c. PICROTOXIN ($C_{12}H_{14}O_5$).

1. Picrotoxin is the poisonous principle of the fruit of ispermum cocculus. It forms white brilliant four-sided p or needles. It is without odor, very bitter, a narcotic p fuses when heated, yielding empyreumatic fumes.

2. Picrotoxin is neutral. It dissolves in water, espe when hot, with tolerable ease, and crystallizes from the tion in needles on cooling and evaporation. Hot alcoho

solves it with extreme facility. The concentrated solution solidifies when cold to a silky mass; more dilute solutions give silky needles when evaporated. Picrotoxin is difficultly soluble in ether. The latter does not withdraw it from aqueous or alkaline solution, but it does withdraw it from acidified solutions (G. GÜNKEL). The ethereal solution when evaporated leaves the picrotoxin in the form of powder or scaly crystals.

3. *Acids* do not neutralize picrotoxin, and, with the exception of acetic acid, do not increase its solubility in water.

4. *Ammonia, potassa* and *soda* dissolve picrotoxin freely. Acids, even carbonic acid, precipitate it from the concentrated solutions. Picrotoxin therefore possesses the character of an acid rather than of a base. The solutions of picrotoxin in potassa or soda, when heated, acquire a yellow or yellowish-red color.

5. If a solution of picrotoxin containing potassa or soda is mixed with a solution of *potassium-copper tartrate* and warmed gently, cuprous oxide separates.

6. *Solutions of iodine, picric acid, tannic acid, and metallic salts* do not precipitate solutions of picrotoxin.

Systematic Course for the Detection of the Alkaloids and of Salicin, Digitalin, and Picrotoxin.

In the methods described under I. and II., it is presupposed that the *non-volatile* alkaloids, etc., are in concentrated solution, dissolved in water by the agency of acids, and free from any substances which would obscure or modify the reactions. Under III. will be described methods to be used in the presence of coloring or extractive matters, and for the detection of *volatile* alkaloids.

I. Detection of the non-volatile Alkaloids, etc., in Solutions containing only one of these Substances.*

§ 239.

1. To a portion of the solution add a drop of dilute sul-

* Where the detection of one of the five more frequently occurring poisonous alkaloids alone is the object, the following simple method, devised by J. ERDMANN, will fully answer the purpose.

In this method, which is more especially applicable in cases where the disposable quantity

phuric acid and then some solution of iodine in p(iodide or of phospho-molybdic acid.

a. No precipitate is formed. Absence of all a possible presence of salicin, digitalin, picrotoxi on to 5.

b. A precipitate is formed. There is cause to the presence of an alkaloid. Pass on to 2.

2. To a portion of the aqueous solution add dilute or soda drop by drop, till the fluid acquires a scar(ceptible alkaline reaction, stir, and allow to stand f time.

a. No precipitate is formed. This is a positive tion, if the solution was concentrated, of the ab all alkaloids; but if the solution was dilute, th(possibility that ATROPIN may be present. Test portions of the solution therefore if necessary a(to § 234 with hydrochlorauric acid, tannic a(heating with sulphuric acid.

of substance is very small, the alkaloids are supposed to be present in the pure the solid form.

1. Treat the substance with 4 or 6 drops of pure concentrated sulphuric acid.

Yellow color, speedily changing to red: VERATRIN.

Rose color, changing afterwards to yellow: BRUCIN.

The other alkaloids, if pure, impart no color to the sulphuric acid. (See HUSEM. ment in opposition, § 227, 5.)

2. No matter whether there is color or not, add to the fluid obtained in 1, 10 or concentrated sulphuric acid mixed with nitric acid (see foot-note to § 226, 7), then of water. After a quarter or half hour the fluid shows:

a. a violet-red color: MORPHIN;

b. an onion-red color: NARCOTIN;

c. a transient red tint, changing to yellow: BRUCIN;

d. the red color of the sulphuric acid solution of VERATRIN is not materially alt(

e. with STRYCHNIN no coloration is observed.

3. Put into the fluid obtained in 2, no matter whether colored or not, 4 or 6 clea of manganese dioxide of the size of a lentil. Within an hour the fluid shows:

a. a mahogany-brown color: MORPHIN;

b. a yellowish-red to blood-red color: NARCOTIN;

c. a transient purple-violet tint, changing to deep onion-red: STRYCHNIN;

d. a transient red tint, changing to gamboge-yellow: BRUCIN;

e. a dark dirty cherry-red color: VERATRIN.

4. Pour the colored fluid obtained in 3, into a test-tube containing 4 times the water, and add ammonia until the neutralization point is *almost* attained. He(avoided as much as possible in these operations.

a. dirty yellow color, changing to brownish-red upon supersaturation with ammo immediate deposition of a notable precipitate: MORPHIN;

b. reddish coloration, more or less intens(according to the degree of dilution; u saturation with ammonia, copious dark-brown precipitate: NARCOTIN;

c. violet-purple colored solution, becoming yellowish-green to yellow upon additi monia in excess: STRYCHNIN;

d. gold-yellow solution, not materially changed by excess of ammonia: BRUCIN

e. faint-brownish solution, turning yellowish upon further addition of ammon depositing a greenish light-brown precipitate: VERATRIN.

b. A precipitate is formed. Add potassa or soda drop by drop till the fluid is strongly alkaline, and if it does not become clear, water also.

α. The precipitate disappears: morphin or atropin. Test a fresh portion of the solution with iodic acid (§ 226, 10).

aa. Separation of iodine: MORPHIN. Confirm by § 226, 7 and 8.

bb. No separation of iodine: ATROPIN. Confirm as in *α*.

β. The precipitate does not disappear: presence of an alkaloid of the second or third group (atropin excepted). Pass on to 3.

3. To another portion of the original solution add two or three drops of dilute sulphuric acid, then a saturated solution of sodium bicarbonate, till the acid reaction just vanishes; stir actively with a glass rod, rubbing the sides of the vessel, and allow to stand half an hour.

a. No precipitate is formed: absence of narcotin and cinchonin. Pass on to 4.

b. A precipitate is formed: narcotin, cinchonin, perhaps also quinin (since its precipitation by sodium bicarbonate is entirely dependent on the amount of water present). To a portion of the original solution add ammonia in excess, then a sufficient quantity of ether, and shake.

α. The precipitate redissolves in the ether, the clear fluid presenting two distinct layers. Narcotin or quinin. To distinguish between them test a fresh portion of the original solution with chlorine water and ammonia. If the solution turns green QUININ is present, if yellowish red, NARCOTIN is present. To confirm for narcotin apply the test with sulphuric acid containing nitric acid (§ 227, 6).

β. The precipitate does not redissolve in the ether: CINCHONIN. To confirm, try the deportment on heating (§ 229, 3) or to potassium ferrocyanide (§ 229, 8).

4. Put a portion of the original substance, or of the residue obtained by evaporating the original solution, in a watch glass, and add concentrated sulphuric acid.

a. A rose-colored solution is obtained, which becomes intensely red upon addition of nitric acid: BRUCIN. Confirm by nitric acid and stannous chloride (§ 232, 6.)

b. A yellow solution is obtained, which gradua yellowish red, blood red, and crimson : VERATRI

c. A colorless solution is obtained, which remai less on standing. Add a fragment of potassium c a deep blue coloration indicates STRYCHNIN, no cl dicates QUININ. Confirm by chlorine water and a

5. To determine whether salicin, digitalin, or picro present, mix a fresh portion of the original solution nic acid.

a. A dirty white flocculent precipitate : DIGITALIN suspected. Test for it with sulphuric acid and water (§ 237, 3.)

b. No precipitate is formed. Make a portion of inal solution barely alkaline with soda solutio solution of copper potassium tartrate, and warm

α. Cuprous oxide is thrown down : PICROTOXIN suspected. Acidify a portion of the original add ether, shake, pour off the ethereal layer, a evaporate. If picrotoxin is present, it will ren may be further tested by § 238.

β. No cuprous oxide is thrown down : SALICIN suspected. Test for it by boiling with dilut chloric acid, etc., according to § 236, 4, and by trated sulphuric acid, according to § 236, 3.

II. DETECTION OF THE NON-VOLATILE ALKALOIDS, SOLUTIONS WHICH MAY CONTAIN ALL THESE SUBSTA

§ 240.

1. Acidify the solution with hydrochloric acid, a ether free from alcohol, shake, pour off the ether, a it to evaporate in a glass dish.

a. No residue remains : absence of digitalin a toxin. Pass on to 2.

b. A residue remains : digitalin and picrotoxin suspected (it must not be forgotten that other su might pass into ethereal solution under these stances, such as oxalic acid, tartaric acid, lac OTTO). Add fresh ether to the aqueous residu again and pour off, in order to remove whatev

uble in ether as completely as possible, and let the ether evaporate. Proceed with the aqueous residue according to 2, and treat the residue of the ether solution, which may contain traces of atropin, as follows:

α. Dissolve a portion in alcohol, and allow the solution to evaporate slowly; long silky needles radiating from a point indicate PICROTOXIN. Confirm according to § 238.

β. Dissolve a portion in concentrated sulphuric acid, and add bromine water. A reddish color indicates DIGITALIN. Confirm by § 237.

γ. Traces of ATROPIN can only be recognized by the property of the aqueous solution of the residue to dilate the pupil.

2. To a portion of the aqueous solution add a solution of iodine in potassium iodide, to another portion add some phospho-molybdic acid.

a. A precipitate is produced in both cases: alkaloids are indicated. Pass on to 3.

b. No precipitate is produced in either case: alkaloids are contra-indicated. Pass on to test for salicin according to § 236.

3. To a small portion of the aqueous solution add potassa or soda till just alkaline, observe whether or no a precipitate is produced, then add potassa or soda in good excess, and dilute.

a. No precipitate was produced by potassa or soda, or a precipitate so produced has redissolved: presence of atropin or morphin, absence of all other alkaloids. Mix a fresh and larger portion of the aqueous solution with sodium bicarbonate in excess, stir, and allow to stand some time.

α. No precipitate is produced: absence of morphin. Shake the fluid with ether, separate the ether, allow it to evaporate, and test the residue for ATROPIN by § 234, 6, 7, 8.

β. A precipitate is produced: MORPHIN. Filter, treat the filtrate according to *α*, to test for atropin, and test the precipitate for morphin according to § 226, 7 and 8.

b. A precipitate was produced by potassa or soda, which would not dissolve in excess of the precipitant or by mod-

erate dilution: treat a larger portion of the ε aqueous fluid like the small portion above, an Proceed with the precipitate according to 4. Sh alkaline filtrate with ether, allow to stand for an h that the morphin which has at first dissolved in th may separate again as completely as possible), ar rate the ether. Allow the ether to evaporate, a the residue for ATROPIN according to § 234, 6, 7, 8. rate the MORPHIN from the aqueous layer by carbo (§ 226, 4) and test it according to § 226, 7 and 8.

4. Wash the precipitate filtered off in 3, *b*, with col dissolve it in slight excess of dilute sulphuric acid, a tion of sodium bicarbonate till the fluid is neutral, stir a rubbing the sides of the vessel, and allow to stand hour.

a. No precipitate is formed: absence of narco cinchonin. Boil the solution nearly to dryness, a up the residue with cold water. If nothing insol mains, pass on to 6; if a residue does remain, ex by 5 for quinin (of which a small amount may be p strychnin, brucin, and veratrin.

b. A precipitate is formed. (This may contain n cinchonin, and quinin, compare § 239, 3, *b*). Filt ceeding with the filtrate according to *a*, with th cipitate as follows: Wash it with cold water, dis a little hydrochloric acid, add ammonia in exce then a sufficient quantity of ether.

α. The precipitate has completely dissolved in th and two clear layers of fluid are formed: absence chonin, presence of quinin or narcotin. Evapor ethereal solution, take up the residue with a lit drochloric acid, add water till the dilution is a 1 : 200, then sodium bicarbonate till neutral, an to stand for some time. A precipitate indicate COTIN: confirm by chlorine water and ammoni by sulphuric acid containing nitric acid (§ 227). orate the clear fluid or the filtrate from the narc dryness, and treat with water. If a residue re wash it, dissolve in hydrochloric acid, and add rine water and ammonia; a green coloration in QUININ.

β. The precipitate has not dissolved in the ether, or not completely: CINCHONIN, perhaps also quinin or narcotin. Filter, and test the filtrate as in *α* for quinin and narcotin; the precipitate consists of cinchonin, and may be further tested according to § 229, 3 or 8.

5. Wash the insoluble residue of 4, *a*, with water, dry it in a water bath, and digest with absolute alcohol.

a. It dissolves completely: absence of strychnin, presence of (quinin) brucin or veratrin. Evaporate the alcoholic solution on the water bath to dryness, and, if quinin has already been detected, divide the residue into two portions, and test one part for BRUCIN, with nitric acid and stannous chloride (§ 232, 6), the other for VERATRIN, by means of concentrated sulphuric acid (§ 233, 6), but if no quinin has as yet been detected, divide the residue into three portions, *a*, *b*, *c*; examine *a* and *b* for BRUCIN and VERATRIN, in the manner just stated, and *c* for QUININ, with chlorine water and ammonia. However, if brucin is present, dissolve *c* in hydrochloric acid, add ammonia and ether, let the mixture stand for some time, evaporate the ethereal solution, and examine the residue for quinin.

b. It does not dissolve, or at least not completely: presence of STRYCHNIN, perhaps also of (quinin) brucin and veratrin. Filter, and examine the filtrate for (QUININ) BRUCIN and VERATRIN, as directed in *a*. The identity of the precipitate with strychnin is demonstrated by the reaction with sulphuric acid and potassium chromate (§ 231, 8).

6. To the rest of the acidified solution which has been exhausted with ether, add more hydrochloric acid and boil for some time. If a precipitate is formed, the presence of SALICIN is indicated. Confirm by adding potassium chromate to the precipitated fluid and boiling (§ 236, 4) and by testing the original substance with concentrated sulphuric acid (§ 236, 3).

III. Detection of the Alkaloids and of Digitalin and Picrotoxin in Presence of Extractive and Coloring Vegetable or Animal Matters.

The presence of mucilaginous, extractive, and coloring matters renders the detection of the alkaloids a task of considerable difficulty. These matters obscure the reactions so

much that we are even unable to determine by a pre experiment whether the substance under examinat tains alkaloids or not. I will now give several met means of which the separation of the alkaloids fr extraneous matters may be effected, and their detecti practicable. Which of these methods to select will upon the particular circumstances of the case.

1. METHOD OF *Stas** FOR THE DETECTION OF P ALKALOIDS (AND OF DIGITALIN AND PICROTOXIN), MODI J. OTTO.†

§ 241.

STAS'S process depends upon the following facts:

α. The acid salts of the alkaloids are soluble and alcohol.

β. The normal and acid salts of the alkaloids erally insoluble in ether. Hence salts of the a do not usually pass into ethereal solution when tral or acid solution is shaken with ether, and he the alkaloids pass into aqueous solution as acid s when the ethereal solution of the pure alkaloid is with dilute sulphuric acid.

γ. If aqueous solutions containing the normal salts of alkaloids are mixed with caustic, carbon bicarbonated alkalies, the alkaloids are liberate now ether or amylic alcohol is added and the mi shaken, the pure alkaloids pass into solution in ter fluid.

It will be evident from the following that there are exceptions to these general rules:

a. If you have to look for alkaloids in the conte stomach or intestines, in food, or generally in matters, mix the substance with twice its we strong pure alcohol, and just enough tartaric acid a decided reaction, and warm to 70° or 75°. Allow thoroughly, filter, and wash with strong pure alcc

* Bull. de l'Académie de Médecine de la Belgique, 9, 304—Jahrb. f. prakt. Pharm Jahresb. Von LIEBIG u. KOPP, 1851. 640.

† Annal. der Chem. u. Pharm., 100, 44—OTTO's Anleit. zur Ausmittel. der Gifte,

If you have to deal with the heart, liver, lungs, or similar organs, cut them into fine shreds, moisten with the acidified alcohol, squeeze, repeat the operation till the substance is exhausted, and filter the mixed fluids.

b. Evaporate the alcoholic fluids at a rather low temperature. This may be done on a water bath, keeping the water at about 80°. The solution under these circumstances will not rise higher than 40° or 50°. If this temperature is considered too high, you may hasten the evaporation by blowing air across the surface of the solution. STAS considers that the temperature should not exceed 35°; he therefore evaporates under a bell glass over sulphuric acid, with or without the aid of an air pump, or in a retort with a current of air passing through it. Such extreme caution, however, is very rarely necessary; at all events, the principal bulk of the fluid may always be evaporated off on a gently heated water bath.

If insoluble substances separate on evaporation (fat, etc.), as indeed is usually the case, filter the now aqueous fluid through a moistened filter, and evaporate the filtrate and washings as above described to the consistence of an extract. If no insoluble substances separate on evaporating the alcoholic fluid, you may, of course, at once evaporate to the consistence of an extract.

c. To the residue left on evaporation, add gradually small portions of cold absolute alcohol, mix intimately, and finally add a large quantity of alcohol, in order to separate everything that can be precipitated by it. Filter the alcoholic extract through a filter moistened with alcohol, wash the residue with cold alcohol, evaporate the alcoholic solution at a low temperature (see above), take up the residue with a little water, neutralize the greater part of the free acid with dilute soda, leaving the solution distinctly acid, and shake with pure ether, free from alcohol and oil of wine (OTTO). By the aid of a separating funnel, or an ordinary burette, separate the ether from the aqueous layer, and wash the latter again and again with fresh ether, until the ether is no longer colored. The ether takes up besides coloring matters also *picrotoxin* and *digitalin* (and *colchicin*). It is advisable to keep the first strongly colored ethereal extract apart from the

subsequent ethereal washings, so that they m
amined separately (compare *h*).

d. Warm the aqueous solution which has be
rated from ether gently, to remove the dissolv
and add solution of soda cautiously, till the flui
distinct reaction with turmeric paper. The alka
thus liberated, *morphin* dissolving in the excess
Shake the fluid with pure ether, and after half
or an hour, separate the two layers of fluid as i
ethereal extract contains *the whole of the alkaloid*
morphin, only a small part of which dissolves in
amount of morphin dissolved by the ether is the
the more completely the acidified aqueous solu
freed from dissolved ether, and the longer the tin
was allowed to elapse between the shaking wi
and the separation of the two layers of fluid.
portion of the ethereal extract to evaporate in
watch glass, which should be heated to about 25
(to prevent condensation of water). If no residue
no alkaloid was dissolved in the ether; pass on
a residue does remain, its appearance will give y
idea of the nature of the alkaloid: thus oily
which gradually collect to a drop, and when
warmed give an unpleasant, suffocating odor, wo
cate a *fluid, volatile base;* while again a solid res
a turbid fluid containing solid particles in sus
would indicate *a non-volatile solid base.* If the
extract has left a residue, repeat the treatment
aqueous fluid with fresh supplies of ether, till a
of the last ethereal washings leaves no residue o
ration. Allow the mixed ethereal extracts to evap
a small glass dish placed upon a bath containing
about 30°, keeping the little dish filled up by t
tion of fresh quantities.

The aqueous fluid which contains the morphin
examined according to *g.*

e. If the acidified aqueous fluid in *c* has been
hausted with ether, on the evaporation of the
extract the alkaloids will remain in so pure a sta
the tests may be applied at once to the residue.
residue consists of oily streaks or drops, compl

evaporation in a vacuum over sulphuric acid, in order to remove the remainder of the ether and ammonia, and then test for *conin* and *nicotin*, according to p. 348. If the residue is crystalline, examine it under the microscope, and then test it according § 239 or § 240, unless the appearance of the crystals should indicate a particular alkaloid. If the residue consists of amorphous rings, dissolve it in absolute alcohol with the aid of a gentle heat, allow the solution to evaporate slowly, observe whether any crystals are thus formed, and then proceed as directed.

f. If, on the contrary, the acidified aqueous fluid in *c* has been insufficiently treated with ether, the residue obtained on the evaporation of the ethereal extract will not be pure enough to be tested at once. In this case dissolve in water slightly acidified with sulphuric acid, filter, if necessary, and shake repeatedly with ether (the ethereal solution may contain the remainder of the *picrotoxin* and *digitalin*, and is to be treated like the ethereal solution obtained in *c*), mix the aqueous solution with potassa in good excess, and shake repeatedly with ether. as prescribed in *d.* Allow the ethereal extracts to evaporate, and proceed with the residue, thus purified, as in *e*;* mix the aqueous fluid, which may contain the remainder of the *morphin*, with the fluid obtained in *d.*

g. The alkaline fluid obtained in *d*, or in *d* and *f*, which must contain the whole or the greater part of the morphin, is treated as follows: Add hydrochloric acid to acid reaction, then ammonia in excess, then without delay pure amylic alcohol, and shake.† As morphin is decidedly more readily soluble in warm amylic alcohol than in cold, it is advisable to dip the flask in warm

* As it appears that strychnin cannot be obtained pure in this way, Fr. Janssens recommends (Zeitschr. f. anal. Chem., 4, 48), to mix the solution in dilute tartaric acid containing foreign substances, with finely powdered sodium bicarbonate, so that the fluid may be acidified with free carbonic acid only If any precipitate is formed, this should be filtered off as quickly as possible. The strychnin is dissolved in the free carbonic acid, and will be precipitated by boiling the filtrate and partially evaporating it. When it has been filtered off and washed, it is dissolved in a small quantity of dilute sulphuric acid (1 : 200), potassium carbonate is added in excess, and the fluid is shaken with six times its volume of ether, which is then poured off and allowed to evaporate.

† Stas recommended ether only for the extraction of alkaloids, while L. v. Uslar and J. Erdmann (Annal. d. Chem. u. Pharm., 120, 121, and 122, 360) prefer the use of amylic alcohol only. However, it is best to employ both menstrua as directed in the text.

water. Separate the two fluids by means of a fun repeat the extraction with fresh quantities of alcohol. Allow the amylic extracts to evapor test the residue for morphin. If the residue is enough, dissolve it in water acidified with sulphu filter, shake with warm amylic alcohol, mix the fluid with ammonia, and shake with amylic alcoh evaporating this amylic extract the *morphin* will pure.

h. The ethereal extracts obtained in *c*, or in have now to be tested for *picrotoxin* and *digitali* extracts also contain coloring matters, which are pally present in the first portions. It is therefor able to evaporate the first portions apart from th portions, and to examine the residues separately.

Warm them with water, and filter the solutio the insoluble matter, which generally has a character. If the solutions possess an acid reacti tralize with some precipitated chalk, evaporate ca to dryness, exhaust the residue with ether, al extract to evaporate, treat the residue again wit and test the aqueous solution thus obtained for *d picrotoxin* and traces of *atropin*, according to § 240 the presence of *colchicin* the aqueous solution wo pear yellow.)

2. Methods of detecting Strychnin, based upon t of Chloroform.*

§ 242.

a. Rodgers' and Girdwood's Method.†

Digest the substance under examination with dilute chloric acid (1 part of acid to 10 parts of water) and evaporate the filtrate on the water bath to dryness, the residue with spirit of wine, evaporate the solutio the residue with water, filter, supersaturate the filtra

* These methods are no doubt useful also for effecting the separation of other however, the deportment of the latter with chloroform has not yet been sufficiently

† Liebig and Kopp's Jahresbericht, 1857, 603. Pharm. Journ. Trans., 16, 497.

ammonia, add 15 grm. of chloroform, shake, transfer the chloroform to a dish by means of a pipette, evaporate on the water bath, moisten the residue with concentrated sulphuric acid, to effect carbonization of foreign organic matters, treat with water, after the lapse of several hours, then filter. Supersaturate the filtrate again with ammonia, and shake it with about 4 grm. of chloroform. Repeat the same operation until the residue left upon the evaporation of the chloroform is no longer charred by sulphuric acid. Transfer the chloroform solution, which leaves a pure residue, drop by drop, by means of a capillary tube, to the same spot on a heated porcelain dish, letting it evaporate, then test the residue with sulphuric acid and potassium chromate. RODGERS and GIRDWOOD succeeded in detecting by this method so small a quantity of strychnin as the $\frac{1}{2000}$ of a grain.

b. METHOD RECOMMENDED BY *E. Prollius.**

Boil twice with spirit of wine, mixed with some tartaric acid, evaporate at a gentle heat, filter the residuary aqueous solution through a moistened filter, add ammonia in slight excess, then about 1½ grm. chloroform, shake, free the deposited chloroform thoroughly from the ley, by decanting and shaking with water, mix the chloroform so purified with 3 parts of spirit of wine, and let the fluid evaporate. If there is any notable quantity of strychnin present, it is obtained in crystals.

c. METHOD RECOMMENDED BY *R. P. Thomas.*†

Acidify slightly with pure acetic acid‡ (sp. gr. 1.04), and digest for several hours at a gentle heat, then strain, press, filter, add potassa in good excess, and shake with chloroform. Separate the chloroform, wash it from potassa, and evaporate; the strychnin will be found in the residue. The morphin remains in the potassa, and may be precipitated gradually by ammonium chloride.

* Chem. Centralbl., 1857, 231.

† Zeitschr. f. anal. Chem., 1, 517. This method includes the detection of morphin.

‡ Acetic acid is recommended, as it also dissolves the tannates of strychnin and morphin.

3. Method of effecting the Detection of Stryc Beer, by *Graham and A. W. Hofmann*.*

§ 243.

This method, which is based on the known fact tha tion of a salt of strychnin, when mixed and shak animal charcoal, yields its strychnin to the charc undoubtedly be found applicable also for the dete other alkaloids. The process is conducted as follows

Shake 30 grm. animal charcoal in 1 litre of the neutral or feebly acid fluid under examination; let th ure stand for from 12 to 24 hours, with occasional filter, wash the charcoal twice with water, then boil an hour with 120 c.c. of alcohol of 80–90 per cent., a loss of alcohol by evaporation. Filter the alcohol h the charcoal, and distil the filtrate; add a few drops tion of potassa to the residual watery fluid, shake wit let the mixture stand at rest, then decant the supernata The ethereal fluid leaves, upon spontaneous evaporat strychnin in a state of sufficient purity to admit of its examination by reagents.

Macadam† employed the same method in his nu experiments to detect strychnin in the bodies of dead a He treated the comminuted matters with a dilute a solution of oxalic acid in the cold, filtered through washed with water, heated to boiling, filtered still war the coagulated albuminous matters, shook with charc proceeded in the manner just described. According statements, the residue left by the evaporation of th holic solution was generally at once fit to be tested for nin. Where it was not so, he treated the residue aga solution of oxalic acid, and repeated the process with charcoal.

4. Separation by Dialysis.

§ 244.

The dialytic method devised by Graham, and descri § 8, may also be advantageously employed to effect the

* Chem. Soc. Quart. Journ., 5, 173. † Pharm. Journ. Trans. 16, 12

ration of alkaloids from the contents of the stomach, intestines, etc. Acidify with hydrochloric acid, and place the matter in the dialyzer. The alkaloids, being crystalloids, penetrate the membrane, and are found, for the greater part, after 24 hours, in the outer fluid; from this they may, then, according to circumstances, either be thrown down at once, after concentration by evaporation; or they may be purified by one of the above described methods.

II.

General Plan of the Order in which Substances should be analyzed for Practice.

§ 245.

It is not a matter of indifference whether the student, in analyzing for the sake of practice, follows no rule or order whatever in the selection of the substances which he intends to analyze, or whether, on the contrary, his investigations and experiments proceed systematically. Many ways, indeed, may lead to the desired end, but one of them will invariably prove the shortest. I will, therefore, here point out a course which experience has shown to lead safely and speedily to the attainment of the object in view.

Let the student take 100 compounds, systematically arranged (*see below*), and let him analyze these compounds successively in the order in which they are placed. A careful and diligent examination of these will be amply sufficient to impart to him the necessary degree of skill in practical analysis. When analyzing for the sake of practice only, the student must above all things possess the means of verifying the results obtained by his experiments. The compounds to be examined ought, therefore, to be mixed for him by a friend who knows their exact composition.

A. *From* 1 *to* 20.

Aqueous solutions of simple salts: *e.g.*, sodium sulphate, calcium nitrate, cupric chloride, etc. These investigations will serve to teach the student the method of analyzing sub-

stances soluble in water which contain but one n
these examples it is only intended to ascertain wha
present in the fluid under examination; but neithe
tection of the acid, nor the proof of the absence of
metals besides the one detected, is required.

B. *From* 21 *to* 50.

SALTS, ETC., CONTAINING ONE METAL AND ONE ACII
METAL AND ONE METALLOID (in form of powder): *e.g*
carbonate, sodium borate, calcium phosphate, arsenic
sodium chloride, hydrogen potassium tartrate, cupri
barium sulphate, lead chloride, etc. These anal
serve to teach the student how to make a prelimina
ination of a solid substance, by heating in a tube o
the blowpipe; how to convert it into a proper form f
sis, *i.e.*, how to dissolve or decompose it; how to d
metal, even in substances *insoluble* in water; and how
onstrate the presence of *one* acid. The detection of
metal and the acid is required, but it is not nece
prove that no other bodies are present.

C. *From* 51 *to* 65.

AQUEOUS OR ACID SOLUTIONS OF SEVERAL METALS. T
vestigations will serve to teach the student the m
separating and distinguishing several metals from eac
The proof is required that no other bases are present
those detected. No regard is paid to the acids.

D. *From* 66 *to* 80.

DRY MIXTURES OF EVERY DESCRIPTION. A portion
salts should be organic, another inorganic; a portion
compounds soluble in water or hydrochloric acid,
insoluble; *e.g.*, mixtures of sodium chloride, calcium
ate, and cupric oxide;—of magnesium ammonium ph
and arsenious oxide;—of calcium tartrate, calcium
and barium sulphate;—of sodium phosphate, ammor
trate, and potassium acetate, etc.

These investigations will serve to teach the stude

to treat mixtures of different substances with solvents; how to detect several acids in presence of each other; how to detect the bases in presence of phosphates of the alkali earth metals; and they will serve as a general introduction to scientific and practical analysis. All the component parts must be detected, and the nature of the substance ascertained.

E. *From* 81 *to* 100.

NATIVE COMPOUNDS, ARTICLES OF COMMERCE, ETC. Mineral and other waters, minerals of every description, soils, potash, soda, alloys, colors, etc.

III.

RECORD OF THE RESULTS OF THE ANALYSES PERFORMED FOR PRACTICE.

§ 246.

The manner in which the results of analytical investigations ought to be recorded is not a matter of indifference. The following examples will serve to illustrate the method which I have found the most suitable in this respect.

PLAN OF RECORDING THE RESULTS OF EXPERIMENTS, NOS. 1–20.

Colorless fluid of neutral reaction.

HCl	H_2S	$(NH_4)_2S$	$(NH_4)_2CO_3$
no precipitate,	*no precipitate*	*no precipitate,*	and NH_4Cl
consequently no	no Pb	no Fe''	*a white precipitate,*
Ag	" Hg''	" Mn	consequently ei-
Hg''_2	" Cu	" Ni	ther Ba, Sr, or
	" Bi	" Co	Ca, no precipi-
	" Cd	" Zn	tate by solution
			of $CaSO_4$, conse-
	" As	" Al	quently CALCIUM.
	" Sb	" Cr^{iv}	Confirmation by
	" Sn		$\bar{O}$
	" Au		
	" Pt		
	" Fe^{iv}		

Plan of Recording the Results of Experiments, Nos. 51–100.

A white powder, on heating, acquires permanent yellow tint, gives no sublimate, emits no visible fumes. Before the blowpipe, a malleable metallic globule, and yellow incrustation, with white border upon cooling. Insoluble in water, effervesces with H Cl, incompletely soluble in that acid, readily soluble in HNO_3 to a colorless fluid.

H Cl	H_2S	$(NH_4)_2S$	$(NH_4)_2CO_3$	No fixed residue upon evaporation.	$Ca(OH)_2$ has failed to evolve NH_3.
White ppt., insoluble in an excess, quite soluble in hot water; H_2SO_4 producing a white ppt. in the solution: LEAD.	Black ppt., insoluble in $(NH_4)_2S_x$, readily soluble in HNO_3. H_2SO_4 produces a white ppt.: LEAD. Examination for Cu, Bi, and Cd: results negative.	White ppt. NH_4OH, applied by itself, produces no ppt.; solution of ppt. in H Cl remains clear upon addition of soda in excess. NH_4Cl no ppt. | H_2S white ppt.: ZINC.	White ppt.; upon dissolving this in HCl and adding solution of $CaSO_4$, a white ppt. forms after some time: STRONTIUM. Precipitation and boiling with $(NH_4)_2SO_4$, filtrate tested for Ca with $\bar{O}$: results negative.		

Of the acids CARBONIC ACID has already been found. Of the remaining acids the following cannot be present:

The preliminary examination has proved the absence of organic acids and HNO_3.

$HClO_3$ cannot be present, because the substance is entirely insoluble in water.

S and H_2SO_4 not, because the substance is readily soluble in HNO_3.

H_2CrO_4 not, as the nitric acid solution is colorless.

H_3PO_4, H_2SiO_3, HF, and $\bar{O}$ not, because the solution filtered from PbS was not precipitated by simple addition of NH_4OH.

H_3BO_3 might be present in trifling quantity; the examination for it gave a negative result.

Cl, I, Br might be present in the form of basic lead compounds. However, $AgNO_3$ has produced no ppt. in the nitric acid solution; accordingly, they cannot be present.

The substance contains, therefore, { metals: LEAD, ZINC, STRONTIUM. / acids: CARBONIC ACID.

NOTES TO TABLE OF SOLUBILITY. (*See* 1

1. Aluminium ammonium sulphate. W.
2. Aluminium potassium sulphate. W.
3. Ammonium arsenic chloride. W.
4. Ammonium platinichloride. W—I.
5. Ammonium sodium phosphate. W.
6. Ammonium magnesium phosphate. A.
7. Ammonium ferrous sulphate. W.
8. Ammonium cupric sulphate. W.
9. Ammonium potassium tartrate. W.
10. Antimony oxychloride. A.
11. Antimony oxide. Soluble in H Cl, not in H N C
12. Antimony sulphide. Soluble in hot H Cl, sl
    HNO_3.
13. Antimony potassium tartrate. W.
14. Bismuth oxychloride. A.
15. Bismuth basic nitrate. A.
16. Calcium sulphantimonate. W—A.
17. Chromic potassium sulphate. W.
18. Cobalt sulphide. Easily soluble in HNO_3, ver
    in H Cl.
20. Iron (ferric) potassium tartrate. W.
21. Manganese dioxide. Soluble in H Cl, insoluble i
22. Mercurius solubilis Hahnemanni. A.
23. Mercurammonium chloride. A.
24. Mercuric sulphate basic. A.
25. Mercuric sulphide. Insoluble in H Cl and in
    Soluble in aqua regia.
26. Nickel sulphide, see cobalt sulphide.
28. Potassium platinichloride. W—A.
29. Silver sulphide. Only soluble in HNO_3.
30. Tin sulphides. Soluble in hot H Cl. Oxidized
    solved by HNO_3. Sublimed stannic sulph
    soluble in aqua regia.
31. Zinc sulphide. Easily in HNO_3, with difficulty

Gold sulphide. Insoluble in H Cl and in HNO_3 ble in aqua regia.

Gold bromide, chloride, and cyanide. w; iodide.

Platinic sulphide. Insoluble in H Cl, slightly so hot HNO_3. Soluble in aqua regia.

Platinic bromide, chloride, and cyanide, nitrate, and sulphate. w; oxide. a; iodide. i.

APPENDIX IV. TABLE OF

W or w—soluble in water. A or a—insoluble in water, soluble in acids (H Cl, H N O_3 and soluble in acids. W—I—sparingly soluble in water and acids. A—I—insoluble in water, sparingly

	Aluminium.	Ammonium.	Antimony.	Barium.	Bismuth.	Cadmium.	Calcium.	Chromium.	Cobalt.	Copper.	Dyad Iron.	Tetrad Iron.
Acetate...	W	W		W	w	w	a	w	w	W	w	W
Arseniate .	a	w	a	a	a	a	a	a	a	a	a	a
Arsenite ..		w	a	a			a		a	A	a	a
Benzoate..	w	w		w		w	w			a	w	a
Borate....	a	w		a	a	w—a	a	a	a	a	a	a
Bromide ..	w	W	w—a	w	w—a	w	w	w & I	w	w	w	w
Carbonate.	a	W		A	A	a	A	a	A	A	A	a
Chlorate ..	w	w		W	w	w	w	w	w	w	w	w
Chloride ..	w	$W_{3\cdot4}$	W—A_{16}	W	W—A_{14}	W	W	W & I	W	W	W	W
Chromate .		w	a	a	a	a	w—a	a	a	w		w
Citrate....	w	w		a		a	w—a	w	w	w	w	W
Cyanide...		w		w—a		a	w	a	a—i	a	a—i	
Ferricy'de.		w					w		i		I	w
Ferrocy'de.		w		w—a			w		i	i	i	I
Fluoride ..	w	W	w	a—i	w	w—a	A	w	w—a	a	w—a	w
Formate ..	w	w		w	w	w	w	w	w	w	w	w
Hydroxide.	A	W	A	W	a	a	W—A	A	A	a	a	A
Iodide	w	W	w—a	w	a	W	w	w	w	w	W	w
Malate....	w	w		w & a			w & a					w
Nitrate ...	w	W		W	W_{15}	w	w	W	W	W	W	W
Oxalate...	a	W	a	a	a	a	A	w—a	A	a	a	a
Oxide.....	A & I		a_{11}	W	a	a	W & A	A & I	A	A	a	A
Phosphate.	a	$W_{5\cdot6}$	w—a	w & a	a	a	W & A	a	a	a	a	a
Silicate ...	A —I			a		a	a	a	a	a	a	a
Succinate .	w—a	w		w—a		w	w—a		w—a	w—a	w	
Sulphate..	$W_{1\cdot2}$	$W_{2\cdot7\cdot8}$	a	A	w	W	W—I	W & A_{17}	W_{18}	W	W	W
Sulphide..	a	W	$A_{12\cdot16}$	W	a	A	W—A	a—i	a	A	A	A
Tartrate ..	w	w_9	a_{13}	a	a	w—a	a	w	w	w	w—a	$W_{?}$

APPENDIX V.—ANALYTICAL TABLES.

The following tables are a useful Synopsis of the Analytical Course for detecting metals. The beginner may study them as an aid in mastering the Scheme of Analysis, but only the more experienced analyst can profitably substitute them for the detailed instructions of the text, as an assistance to the memory in the execution of analyses.—EDITOR.

Tables for the Detection of Metals in Solutions.

Table I., Separation into Groups.

Table II., for Group V., 1st Division.

Table III., for Group V., 2d Division, and Group VI.

Table IV., for Groups IV. and III., when Phosphates, Borates, etc., are absent.

Table V., for Groups IV. and III., when Phosphates, Borates, etc., are present.

Table VI, for Group II.

Table VII., for Group I.

TABLES FOR THE DETECTION OF METALS IN SOLUTIONS.

TABLE I.—SEPARATION INTO GROUPS.

Add H Cl and filter.

Precipitate.	*Filtrate.* Pass H_2S and filter.			
	Precipitate.	*Filtrate.* Add NH_4Cl, NH_4OH and $(NH_4)_2S$ and filter.		
		Precipitate.	*Filtrate.* Add $(NH_4)_2CO_3$ and filter.	
			Precipitate.	*Filtrate.*
AgCl	PbS	NiS	$BaCO_3$	Mg
Hg_2Cl_2	HgS	CoS	$SrCO_3$	K
$PbCl_2$	Bi_2S_3	FeS	$CaCO_3$	Na
	CuS	MnS		NH_4
Wash and examine according to Table II.	CdS	ZnS		
	SnS	$Cr_2(OH)_3$	Wash and examine according to Table VI.	Examine according to Table VII.
	SnS_2	$Al_2(OH)_3$		
	Sb_2S_3			
	As_2S_3	Certain salts of Ba Sr Ca Mg and SiO_2		
	Wash and examine according to Table III.			

Table II.—Group V., Div. I.

Treat on the filter with hot water.

Filtrate.	*Residue.* Treat on the filter with NH_4OH.	
	Filtrate.	*Residue*
Add H_2SO_4.	Add excess of HNO_3.	
White p. = **Pb.**	White p. = **Ag.**	is black = **Hg''_2.**

Table III.—Group V., Div. II., and Group VI.

Warm with $(NH_4)_2S$ and filter.

Residue. Wash, boil with strong HNO_3, dilute and filter.

Filtrate. Add H_2SO_4 dil., evaporate on water bath till HNO_3 is expelled, take up with H_2O and filter.

Filtrate. Add HCl in excess, filter, wash and dry the p. Fuse with Na_2CO_3 + $NaNO_3$ and extract with H_2O.

Residue.
Divide in 2 parts.

1. Dissolve in HCl + $KClO_3$, and add $SnCl_2$. A gray or white p. = **Hg''**.
2. Fuse with $KCy + Na_2CO_3$. If metallic globules, wash them, and treat with HNO_3.

p.	Add H_2SO_4.
Wash, boil with strong HCl, pour off acid, add H_2O and then H_2S. A yellow p. = **Sn.**	p. = **Pb.**

Residue. = **Pb.**

Filtrate. Add excess of NH_4OH, warm and filter.

Precipitate.	*Filtrate.* (If blue, **Cu** is present.) Add H_2S, wash p., boil it with H_2SO_4 dil., filter off CuS, and add H_2S. A yellow p. = **Cd.**
Wash, dissolve in watch-glass in least quantity of HCl, and add H_2O. Milkiness = **Bi.**	

Residue. Wash with dilute alcohol, treat with HCl and Zn in contact with Pt. Black stain = **Sb.** Decant liquid, add to it $HgCl_2$. White or gray p. = **Sn.** Test residue for **Pt.** and **Au.**

Solution. Acidify with HNO_3, add $AgNO_3$, filter, neutralize with dilute NH_4OH. Red-brown p. = **As.**

TABLE V.—GROUPS IV. AND III.

When Phosphates, Borates, Oxalates, and Silicates are present.

Treat with cold dilute HCl, and filter.

Residue. Wash, test a portion in metaphosphate bead.

A skeleton = SiO_2.
A blue bead = **Co**.
A yellow bead = **Ni**.

If a blue bead, dry, filter, incinerate, dissolve ash in $HCl + HNO_3$, nearly neutralize with NaOH, add KNO_2, and acetic acid till acid, allow to stand, filter off yellow p. To f. add NaOH, filter and test p. in borax bead for **Ni**

Filtrate. Boil to expel H_2S, filter, if necessary, and divide in 2 parts.

1. Add dilute H_2SO_4 and filter. Wash and examine the *precipitate* for **Ba** and **Sr**. Mix the *filtrate* with three volumes of alcohol, collect the p., dissolve in H_2O, and test for **Ca** with $(NH_4)_2C_2O_4$.

2. Add strong HNO_3 and boil. Test a small portion for **Fe** with KCNS. To the rest add Fe_2Cl_6, till a drop gives a yellow p. with NH_4OH, evaporate to small bulk, add H_2O, nearly neutralize with Na_2CO_3, add excess $BaCO_3$, allow to stand, filter.

Precipitate. Wash and divide in two parts.

1. Boil with Na_2OCl_2 and filter. A yellow f. = **Cr**.

2. Boil with NaOH and filter. To f. add NH_4Cl, and boil. Test p. for SiO_2 in metaphosphate bead. If SiO_2 is present, ignite rest of p., fuse with $K_2S_2O_7$, treat with HCl, and filter; to f. add NH_4OH. A p. = **Al**.

Filtrate. Add HCl, boil to expel CO_2, add NH_4OH and $(NH_4)_2S$. Filter.

Precipitate. Wash with H_2O and a little $(NH_4)_2S$, treat with acetic acid and filter.

Residue. Wash, treat with dilute HCl, and filter.* Treat with HNO_3, evaporate, add NaOH, boil, and filter.* To f. add $(NH_4)_2S$. A white p. = **Zn**.

Filtrate. Add NaOH, boil, filter, and test p. for **Mn**.

Filtrate. Add H_2SO_4, boil, filter off $BaSO_4$, add excess NH_4OH, then $(NH_4)_2C_2O_4$, filter off CaC_2O_4, and test for **Mg**.

* If a residue, test for Ni and Co.

TABLE VI.—GROUP II.

Dissolve in H Cl, evaporate to dryness on the water bath. Dissolve a portion of the residue in a little water, to the solution add $CaSO_4$, and allow to stand.

No precipitate is formed. Dissolve rest of residue in water, and add $(NH_4)_2C_2O_4$. A p. = **Ca.**

A precipitate is formed after some time. = **Sr.** Dissolve rest of residue in water, boil with $(NH_4)_2SO_4$ and NH_4OH for some time, filter off $SrSO_4$, and to f. add $(NH_4)_2C_2O_4$. A p. = **Ca.**

A precipitate is formed immediately. = **Ba.** Digest rest of residue with alcohol, powdering it in the dish with a pestle, filter off the $BaCl_2$, to f. add H_2SO_4, and filter. Boil p. with $(NH_4)_2SO_4$ and NH_4OH for some time and filter.

Residue. **Test for Sr.** on platinum wire in Bunsen flame.

Filtrate. Dilute and add $(NH_4)_2C_2O_4$. A p. = **Ca.**

Table VII.—Group I.

To a portion of the solution add Na_2HPO_4, stir well, and allow to stand. A crystalline p. = **Mg.**

If Mg is absent. Evaporate rest of solution to dryness, ignite on piece of porcelain till white fumes cease, dissolve the residue in the least quantity of water, filter if necessary into a watch glass, and test for K and Na as below.

If Mg is present. Evaporate rest of solution to dryness, ignite till white fumes cease, warm residue with a little water, add $Ba(OH)_2$ till alkaline, boil, filter, to f. add $(NH_4)_2CO_3$, warm gently, filter, evaporate f., ignite, dissolve residue in least quantity of water, add a drop of HCl, pour solution into watch glass, and test it for K and Na as below.

Dip a clean platinum wire into the solution, and hold it in Bunsen flame, a yellow color = **Na.** Then add H_2PtCl_6 to the solution and stir; a yellow p. = **K.** If no p., evaporate to dryness on water bath, add a drop or two of water, and observe whether yellow powder remains undissolved.

Warm the original substance with NaOH in a test tube. A smell of NH_3 = **NH_4.**

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